15. Delayed Fluorescence from Upper Excited Singlet States S_n ($n > 1$) of the Aromatic Hydrocarbons 1,2-Benzanthracene, Fluoranthene, Pyrene, and Chrysene in Methylcyclohexane

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Summary

Delayed fluorescence (DF.) spectra of 1,2-benzanthracene, fluoranthene, pyrene, and chrysene in methylcyclohexane were measured at $-80°$ up to the wavenumber corresponding to the energy of two triplets. With all four compounds a weak DF. $S_n \rightarrow S_0$ from the highest state S_n accessible by triplet-triplet annihilation (TTA) was found. Lifetimes of S_n calculated (a) from the ratio of the DF 's $S_n \rightarrow S_0$ and $S_1 \rightarrow S_0$ and (b) from the difference in line-width of the 0,0-transitions $S_{n,0} \leftarrow S_{0,0}$ and $S_{1,0} \leftarrow S_{0,0}$ agree reasonably well. This indicates that population of the highest accessible excited singlet state is the dominating primary process in the excited singlet channel of TTA. There is no evidence for excimer formation being the first step in TTA. DF. spectra extend up to the energy of two triplets. With pyrene the intensity distribution in the hot-band region of the DF. $S_2 \rightarrow S_0$ suggests that in TTA the same vibrational selection rules are valid as in one-photon absorption $S_2 \leftarrow S_0$ and that vibrational relaxation within the S_2 manifold is slow compared with internal conversion $S_2 \rightsquigarrow S_1$. The experimental technique is described in detail and experimental difficulties arising from impurities and photoproduct formation are discussed.

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1. Introduction. - The delayed fluorescence (DF.) of aromatic hydrocarbons is a well known phenomenon [1-3] which has been found in solutions [1], in the gasphase [4], in molecular crystals [5] [6], and in polymers of the type of polyvinylnaphthalene [7]. It is due to the population of the lowest excited singlet state S_1 by the bimolecular interaction of molecules in the lowest excited triplet state T_1, by so-called triplet-triplet annihilation (TTA) $T_1 + T_1 \rightarrow S_1 + S_0$ [1]. Different steps may be distinguished in the process leading to the DF. $S_1 \rightarrow S_0$:

a) Formation of an encounter complex ($T_1 \ldots T_1$) with singlet, triplet, and quintet character [8]:

$$T_{1,e} + T_{1,e} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^{1,3,5}(T_{1,e} \ldots T_{1,e}) \qquad (1)$$

The subscript e indicates that the molecules in T_1 are in thermal equilibrium with respect to their vibrational energy.

b) Transition of the encounter complex into an excited singlet or triplet or quintet dimer state (S_n or T_x or Q_p) if such states are energetically accessible:

$$
{}^{1,3,5}(T_{1,e}\cdots T_{1,e}) \left\langle \begin{array}{ll}
\xrightarrow{k_S} {}^1(S_{n,v}\cdots S_{0,v'}) & \qquad (2a) \\
\xrightarrow{k_T} {}^3(T_{x,v}\cdots S_{0,v'}) & \qquad (2b) \\
\xrightarrow{k_Q} {}^5(Q_{p,v}\cdots S_{0,v'})\,. & \qquad (2c)
\end{array} \right.
$$

The subscript v is used to indicate that the excited dimer[1]) is not in thermal equilibrium with respect to vibrational energy.

c) Internal conversion (IC.) of the excited dimer state into the lowest excited state of the respective multiplicity and vibrational energy relaxation (VR). In the case of the excited singlet dimer state for $n > 1$:

$$ {}^1(S_{n,v}\cdots S_{0,v'}) \xrightarrow{k_{IC}} {}^1(S_{1,\bar{v}}\cdots S_{0,v'}) \qquad (3) $$

$$ {}^1(S_{1,\bar{v}}\cdots S_{0,v'}) \xrightarrow{k_{VR}} {}^1(S_{1,e}\cdots S_{0,e})\,. \qquad (4) $$

d) Dissociation of the excited dimer or formation of an excimer (MM)*. In the case of an excited singlet dimer state:

$$
{}^1(S_{1,e}\cdots S_{0,e}) \left\langle \begin{array}{ll}
\longrightarrow S_{1,e} + S_{0,e} & \qquad (5a) \\
\longrightarrow {}^1(MM)_e^*\,. & \qquad (5b)
\end{array} \right.
$$

e) Emission of the DF of excited monomers and of excimers:

$$ S_{1,e} \rightarrow S_{0,v} + h\nu_{mon} \qquad (6a) $$

$$ {}^1(MM)_e^* \rightarrow {}^1(MM)_v + h\nu_{exim}\,. \qquad (6b) $$

In the present paper attention is focussed onto the primary process of excited singlet state formation by TTA. With many aromatic hydrocarbons the energy of two triplet states T_1 is sufficient for primary population of upper excited singlet states S_n ($n > 1$). In principle a primary population of S_n can be demonstrated by the measurement of a DF. $S_n \rightarrow S_0$. Indeed with 1,2-benzanthracene and with fluoranthene a DF. from the highest excited states S_n accessible by TTA was found [9]. This work has been continued, and in this paper new results are reported and discussed in detail:

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[1]) Strictly speaking the DF. of aromatic hydrocarbons is always emitted by pairs of interacting molecules (*cf.* Sect. 4.2). Referring to this interaction in a general way the term "excited dimer" is used, the interaction ranging from zero to "excimer" interaction in the restricted sense.

(1) In the first experiments paraffin oil was taken as solvent for reasons given in [9]. A viscous solvent such as paraffin oil has several disadvantages: Because of the strong temperature dependence of the viscosity the useful temperature range is rather small, temperature control is difficult at high excitation intensity, and continuous or periodic renewal of a sample (which is necessary because of photochemical degradation of a sample at high excitation intensity) is also difficult. Therefore in all subsequent work solvents with sufficiently low viscosity were used. The preferred solvent was methylcylohexane (MCH) which is a sufficiently good solvent for most aromatic hydrocarbons and has a low melting point (– 127°). The measurement of the DF. from upper excited singlet states of 1,2-benzanthracene and fluoranthene was repeated with MCH as solvent at – 80°.

(2) The investigation was extended to other compounds. Up to now a DF. $S_n \rightarrow S_0$ from the highest state S_n accessible by TTA was found with all compounds with which a strong DF $S_1 \rightarrow S_0$ was found (the numbering of S_i ($i = 1, 2, \ldots$) is phenomenological and refers to the succession of apparently different electronic transitions in the one-photon absorption spectrum): With 1,2-benzanthracene (S_3), fluoranthene (S_4), pyrene (S_2), chrysene (S_3), naphthalene (S_2), phenanthrene (S_3), triphenylene (S_3), and *N*-methylcarbazol (S_4). In the present paper results obtained with the first four compounds are communicated. For comparison prompt $S_1 \rightarrow S_0$ fluorescence spectra and absorption spectra were measured under the same experimental conditions.

(3) If different excited singlet states S_i ($i = 1, 2, \ldots, n$) can be populated by TTA then the relative probabilities P_i for primary population of S_i are of interest. With the assumption $P_n = 1$ a lower limit for the lifetime of S_n can be determined. By comparison of this value with an independent estimate of the lifetime of S_n it can be shown that indeed primary population of S_n by TTA is one of the dominating processes (2 a).

(4) The DF. is - strictly speaking - always the fluorescence of pairs of interacting molecules. Nevertheless the observed DF. $S_n \rightarrow S_0$ has the character of a monomer fluorescence. The consequences of this observation will be discussed.

(5) A general feature of the fluorescence from very short-lived excited states is that even in condensed phase the emitting molecules are not in thermal equilibrium with respect to their vibrational energy. Therefore the fluorescence spectrum in general will depend on the primarily populated vibronic states $S_{n,v}$ and relatively strong hot-band fluorescence $S_{n,v} \rightarrow S_{0,v'}$ (vibrational energy $E_v > E_{v'}$) will be the rule. Conversely, from the intensity distribution in the hot-band region of the DF. $S_n \rightarrow S_0$ some information can be obtained on vibrational selection rules in TTA (2 a).

(6) The DF. from upper excited singlet states S_n is typically 10 000 times weaker than the DF. $S_1 \rightarrow S_0$. Consequently the measurement of the DF. $S_n \rightarrow S_0$ is connected with experimental difficulties. Therefore the experimental technique will be described in some detail and difficulties arising from the presence of impurities will be discussed.

2. Experimental Section. - 2.1. *Substances.* 1,2-Benzanthracene, fluoranthene[2]), pyrene[2]), and chrysene were purified by the following procedures: Polar or only slightly soluble impurities were removed by column chromatography (10 to 30 g of aromatic hydrocarbon per 300 g adsorbent, aluminium oxide *Woelm* W 200 basic, cyclohexane, 70°, N_2-atmosphere); fluoranthene[2]) and pyrene[2]) additionally were treated with maleic acid anhydride in benzene at 80° in order to remove impurities forming *Diels-Alder* adducts and were chromatographed a second time. After sublimation i.V. the substances were sealed in glass tubes under a N_2-atmosphere and zone-refined in a vertical zone-refiner. Methylcyclohexane was purified chromatographically (silica gel *Woelm* + aluminium oxide *Woelm* W 200 basic) and rectified over a 800 mm column.

The purity of the aromatic hydrocarbons was tested by mass spectrometry which allows the detection of small amounts of impurities with higher molecular mass M[3]). Pyrene ($C_{16}H_{10}$, $M \simeq 202$) still contained about 1% of an impurity with $M' \simeq 208 = 202 + 6$, and chrysene ($C_{18}H_{12}$, $M \simeq 228$) still contained about 5% of an impurity with $M' \simeq 234 = 228 + 6$. At first it was supposed that the impurities might be the hexahydro-compounds. However, the impurities could not efficiently be removed by treatment with a dehydrogenating agent (tetrachloro-*p*-benzoquinone in boiling toluene [11]) and subsequent column chromatography. Elementary analysis revealed the presence of sulfur. In the case of pyrene the impurity is probably phenanthro[4,4',4'',5-*bcd*]thiophene [12], that is a pyrene in which an etheno bridge –CH=CH– ($M \simeq 26$) has been replaced by a sulfur atom ($M \simeq 32$). Thiophene derivatives of this type are easily converted into sulfones by oxidation with hydrogen peroxide in glacial acetic acid [12]; the sulfones are easily separated by column chromatography. By this method the sulfur containing impurities of chrysene (and *e.g.* also of phenanthrene which usually contains several percent of dibenzthiophene) are removed. With pyrene this method works less satisfactorily because pyrene is oxidized too easily by hydrogen peroxide. However, it was possible to remove the sulfur containing compound completely by column chromatography (2 g pyrene per 300 g aluminium oxide *Woelm* W 200 (activity grade Super I), hexane, 50°).

The purity of methylcyclohexane (MCH) was sufficient for the investigation of the DF of the following aromatic hydrocarbons (the wave numbers of the corresponding triplet energies $E(T_1)$ are given in brackets): 1,2-Benzanthracene (16 800 cm^{-1}), pyrene (17 000 cm^{-1}), fluoranthene (18 500 cm^{-1}), chrysene (20 000 cm^{-1}), naphthalene (21 300 cm^{-1}), and phenanthrene (21 600 cm^{-1}). With triphenylene (23 300 cm^{-1}) and *N*-methylcarbazole (24 000 cm^{-1}) in MCH no DF. was found, in heptane, however, a DF. was found without difficulty. Therefore it is suspected that the purified MCH still contained an impurity with $21\,600\ cm^{-1} < E(T_1) < 23\,300\ cm^{-1}$.

2.2. *Samples.* The measurement of a very weak DF. requires intense and prolonged excitation of a sample. Therefore photochemical degradation of samples is a major problem in this kind of work. This problem is less severe if only a small fraction of a large volume is irradiated and the photoproducts continuously are diluted over the whole volume. This can be achieved with the glass apparatus shown in *Fig. 1.* The variant (a) is used for excitation with an arc lamp, the variant (b) for excitation with a laser. The glass apparatus was connected with a cryostat (*Lauda* UK-80 DW). If the temperature of the solution in tube (c) is lower than in tube (d) then in general the solution will circulate in the indicated direction. At a cryostat temperature of – 80° and with heating of the solution by ambient air the temperature measured with a thermocouple was – 79.5° below the suprasil capillary of variant (a) and – 78° left to the fluorescence flow cell (rectangular cross-section 3 mm × 10 mm) of variant (b). Solutions were degassed with the usual freeze-pump-thaw technique. The concentration of the aromatic hydrocarbon was sufficiently low in order that fluorescence reabsorption could be neglected.

2.3. *Measurement of fluorescence spectra.* Samples were excited either with a mercury-xenon arc lamp (*Hanovia* 977-B1, 1000 Watt) in combination with filters (inorganic salt solutions [13] and *Schott* glass filters) and an *Ebert* grating monochromator (*Jarrell Ash,* focal length 250 mm, for measurement of prompt fluorescence (PF.) spectra and of the DF. spectrum of chrysene) or with the UV.-lines of an argon ion laser (*Spectra-Physics* model 171-03). The advantages of laser excitation

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[2]) Thanks are due to Dr. *L. M. Peter* (formerly *Fritz-Haber*-Institut in Berlin, now University of Southampton) for samples of carefully purified fluoranthene and pyrene (with respect to triplet quenchers [10]).

[3]) Thanks are due to Dr. *W. Kühnle* for suggesting and performing the mass spectrometric investigation.

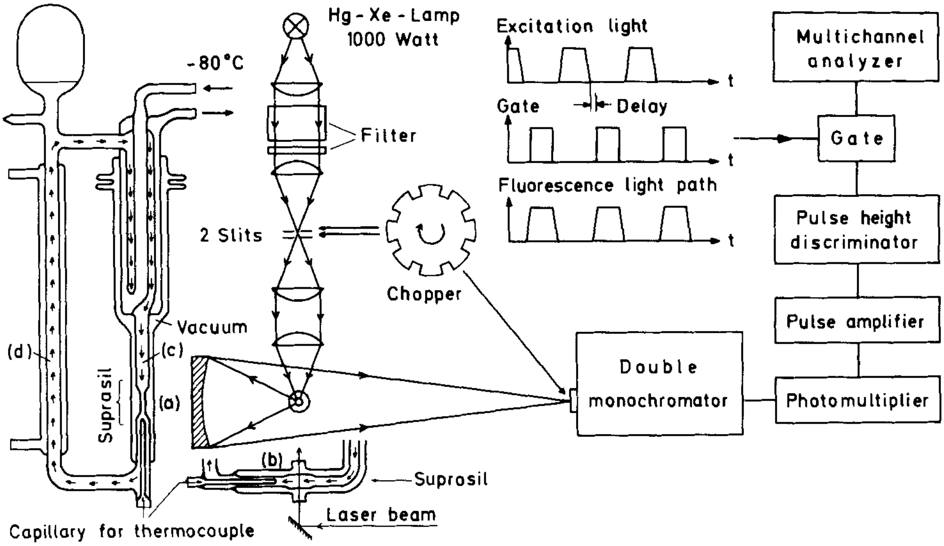

Fig. 1. *Experimental set-up for the measurement of DF. spectra.* The inner diameter of the suprasil quartz glass capillary of variant (a) of the glass apparatus was about 3 mm, the cross-section of the fluorescence flow cell of variant (b) was 3 mm × 10 mm.

are discussed in Sect. 2.5. Fluorescence spectra were measured with a grating double monochromator (two coupled *Jarrell Ash Ebert* monochromators, focal length 250 mm, additive dispersion) and with cooled photomultipliers (*EMI* 6256, blue-sensitive, dark current $\simeq 4$ pulses/s, and *EMI* 9658 R, red-sensitive, dark current $\simeq 50$ pulses/s). The width of the central slit of the double monochromator was constant and equal to 6 mm, corresponding to a spectral width of 9.6 nm with the UV.-gratings and of 19.2 nm with the VIS.-gratings. Therefore the transmission factor for 'near' instrumental stray light was much higher than for 'far' instrumental stray light. For this reason the intensity distribution in the hot-band region of the DF. $S_1 \rightarrow S_0$ is possibly not quite correct. The photon counting technique was used and spectra were recorded with a multichannel-analyser. The monochromator was driven by a synchromotor with a special gear (*Halstrup* D 64, 1 rpm in forward direction, 10 rpm in backward direction). Channel advance pulses were derived from line frequency (50 Hz). The starting wavelength was reproduced mechanically by a microswitch with an accuracy better than ± 0.05 nm. The spectral sensitivity of the fluorimeter was determined in the spectral range from 280 nm to 800 nm with a quartz-iodine-tungsten lamp of known intensity distribution and with a white reflectance standard (*Eastman Kodak* 6091) replacing the sample. In the spectral range from 220 nm to 280 nm the relative intensity of incident monochromatic light was determined with rhodamine B in ethylene glycol (4 g/l) as a quantum counter.

For measurement of DF. spectra the excitation light and the fluorescence light were chopped by two mechanical choppers. The chopping frequency was up to 1000 Hz (50 rps, up to 20 segments). The relative phase of the two choppers was adjusted by rotation of one of the two synchromotors. Stray excitation light was effectively suppressed by use of two chopper blades and two slits in the excitation light path and by an electronic gate in the photon counting device which was closed during excitation *(Fig. 1)*. Apart from the suppression of stray excitation light the electronic gate has two additional advantages: The measured dark current is reduced to about 1/3, and small spectral shifts - produced by the inequality of the DF. intensities during opening and closing of the fluorescence light path - are avoided. The last point is essential for determination of the delayed excimer fluorescence spectrum by subtraction of the PF. spectrum from the DF. spectrum. The $S_1 \rightarrow S_0$ PF. spectra were measured under exactly the same experimental conditions (apart from excitation intensity).

For measurement of the spectrum of a very weak DF. the monochromator was scanned up to several 100 times and the single spectra were accumulated in the multichannel analyser. The constancy of the spectrum was checked. The intensity range of the complete DF. spectra extended over 6 to 7 orders of magnitude. Therefore the complete DF. spectra had to be composed of sections measured at different excitation intensities.

2.4. *Evaluation and representation of data.* The measured fluorescence spectra consisted of equidistant points with respect to the wavelength λ. The following corrections were performed: *a)* The maximum counting rate of the multichannel analyser (*Ortec* 6220) for equidistant pulses was $f_{max} \simeq 6 \cdot 10^6$ Hz. Because of the limited counting rate and consequently limited pulse pair resolution not all pulses are counted. With N_c the number of counted pulses per channel and t the total measuring time per channel, the true number of pulses per channel, N, was obtained with the formula $N = N_c[1 + N_c/(f_{max}\ t)]$. For $N_c \ll f_{max} \cdot t$ the correctness of the formula follows from statistical considerations. By computer simulation of photon counting it can be shown [14] that the formula is practically useful for $N_c \lesssim 0.1 \cdot f_{max} \cdot t$.

b) The dark current N_d was subtracted.

c) Finally the correct relative intensities $I(\lambda)$ were obtained by division of $(N(\lambda) - N_d)$ by the relative spectral sensitivity $S(\lambda)$ of the fluorimeter.

For representation of a fluorescence spectrum as a function of the wavenumber $\tilde{\nu}$ the relative intensities $I(\lambda)$ were multiplied by λ^2 and equidistant points ($\Delta\tilde{\nu} = 20$ cm^{-1}) with respect to wavenumber $\tilde{\nu}$ were interpolated by a third order polynomial. Absorption spectra were measured with a wavelength calibrated *Cary*-17 absorption spectrometer. Absorbances $E(\lambda)$ were read point by point, the density of points depending on the vibrational structure. The wavelengths were corrected and equidistant points ($\Delta\tilde{\nu} = 20$ cm^{-1}) with respect to wavenumber $\tilde{\nu}$ were interpolated by a third order polynomial. All spectra were plotted with a *Calcomp* plotter.

2.5. *Experimental difficulties.* The measurement of very weak fluorescences from upper excited singlet states is connected with difficulties [15]. Some of the typical difficulties are less serious or even completely absent in the case of DF. from upper excited singlet states. In this section difficulties arising from the presence of impurities and from the formation of photoproducts are discussed. Impurities Q of an aromatic hydrocarbon M can be classified according to the energies $E(^1Q^*)$ and $E(^1M^*)$ of the lowest excited singlet state and the energies $E(^3Q^*)$ and $E(^3M^*)$ of the lowest excited triplet state:

a) $E(^1Q^*) < E(^1M^*)$ and $E(^3Q^*) < E(^3M^*)$: Examples are Q = tetracene and M = anthracene; Q = anthracene and M = phenanthrene; Q = anthracene and M = carbazole.

Impurities of this type are easily detected by the absorption spectrum, by the fluorescence $^1Q^* \rightarrow {}^1Q$ and by the phosphorescence $^3Q^* \rightarrow {}^1Q$ of an impure crystal of M, and by the DF. $^1Q^* \rightarrow {}^1Q$ of a solution of M. Removal of impurities of this type is essential for the investigation of spectroscopic properties of "pure" molecular crystals. Efficient purification procedures [16] were developed, and the efficiency of a purification procedure can be checked easily. For the investigation of the fluorescence $S_n \rightarrow S_0$ from upper excited singlet states S_n of a compound M impurities of type (a) are not particularly harmful because there is no danger that a fluorescence $S_1(Q) \rightarrow S_0(Q)$ is interpreted as a fluorescence $S_n(M) \rightarrow S_0(M)$.

b) $E(^1Q^*) > E(^1M^*)$ and $E(^3Q^*) < E(^3M^*)$: An example is Q = pyrene and M = fluoranthene. Impurities Q of type (b) are easily detected by the phosphorescence $^3Q^* \rightarrow {}^1Q$ of an impure crystal of M [17] and by the DF. $^1Q^* \rightarrow {}^1Q$ of a solution of M [2]. The dangerousness of impurities of type (b) (or type (d)) is illustrated by a recent paper [18], in which the obvious fluorescence $S_1 \rightarrow S_0$ of an impurity of fluoranthene (possibly of pyrene or a pyrene derivative) is interpreted as a PF. $S_2 \rightarrow S_0$ of fluoranthene.

c) $E(^1Q^*) < E(^1M^*)$ and $E(^3Q^*) > E(^3M^*)$: An example is Q = fluoranthene and M = pyrene. The typical triplet sensitizers are impurities of type (c). Impurities of type (c) can be detected by absorption spectroscopy, by the time-dependence of the spectrum and the intensity of the DF., and by triplet-triplet absorption spectroscopy [19]. For the investigation of a DF. $S_n(M) \rightarrow S_0(M)$ the presence of an impurity of type (c) is in general not harmful, even if the energy transfer $^3Q^* + {}^1M \rightarrow {}^1Q + {}^3M^*$ is not complete.

d) $E(^1Q^*) > E(^1M^*)$ and $E(^3Q^*) > E(^3M^*)$: Examples are Q = phenanthro[4,4',4'',5-*bcd*]thiophene and M = pyrene (*cf.* Sect. 2.1); Q = dibenzothiophene and M = phenanthrene; Q = carbazole and M = anthracene.

The detection of small amounts of impurities of type (d) by fluorescence or phosphorescence spectroscopy is difficult. Impurities of type (d) are particularly dangerous in the investigation of the

PF. from low lying states $S_n(M)$ (n > 1). In the investigation of the DF. $S_n(M) \rightarrow S_0(M)$ the dangerousness of the impurity of type (d) depends on experimental conditions. If the energy transfer $^3Q^* + {}^1M \rightarrow {}^1Q + {}^3M^*$ is sufficiently fast (*i.e.* if the solvent viscosity is low and the concentration of M is high) or if Q is not excited at all ($E(^1M^*) \leq h\nu < E(^1Q^*)$) the presence of Q may cause no trouble.

e) $E(^1Q^*) \geq E(^1M^*)$ and $E(^3Q^*) \simeq E(^3M^*)$: The spectroscopic detection of an impurity Q of type (e) is difficult. Possibly 1,2-benzanthracene contains an impurity of this type. The decay curve of the DF. $S_1 \rightarrow S_0$ of 1,2-benzanthracene in MCH and in hexane at 25° consisted of a fast component (which was not due to 2nd order decay by TTA) and a slow component [20]. The spectra of PF. and DF. $S_1 \rightarrow S_0$ were identical.

The discussion of different types of impurities is concluded with a warning with regard to the efficiency of zone melting. From the fact that some known impurities of a given substance are easily separated by zone melting often the general conclusion is drawn that a high number of zone passes guarantees a high purity of a substance. Of course in general this is not true. If the separation of an impurity by zone melting is theoretically possible [21] [22] the actual efficiency of purification by zone melting strongly depends on the zone melting device [22]. The efficiency of zone melting devices of the vertical type seems to be rather low [22]. With a horizontal zone melting tube a separation efficiency comparable with the theoretically possible efficiency can be achieved [22].

The difficulties arising from the photodegradation of a sample are of three different types:

1) Photodegradation limits the total measuring time. Photodegradation is kept to a minimum by laser excitation and by suitable choice of excitation wavelength. With laser excitation a higher fraction of the total emitted DF. can be measured than with arc lamp excitation. Photodegradation is due to photodimerization and to other photochemical reactions. Photodimerization is an inevitable concomitant of TTA in fluid solutions. The probability of other photochemical reactions may depend on photon energy and excitation intensity. In general the probability of monophotonic irreversible photoreactions increases with increasing photon energy. For this reason and also with respect to the probable presence of impurities of type (d) the best would be to excite a compound in the 0,0-transition of $S_1 \leftarrow S_0$. However, with most aromatic hydrocarbons the transition $S_1 \leftarrow S_0$ is rather weak ($\varepsilon < 1000$ M^{-1} cm^{-1}) and moreover the 0,0-transition usually does not coincide with one of the available excitation lines. Excitation in a weak absorption band may be disadvantageous if incidentally this band coincides with a strong band in the triplet-triplet absorption spectrum. Under the conditions of the measurement of a DF. from upper excited singlet states a substantial fraction of the aromatic hydrocarbon is in the triplet state. Therefore triplet-triplet absorption followed by irreversible photoreactions may considerably contribute to the photochemical degradation of a sample.

2) Deposition of photoproducts on the walls of the fluorescence cell: During prolonged excitation of a sample always photoproducts of low solubility, *e.g.* photodimers, are formed and deposited preferentially near the window through which the excitation light enters the fluorescence cell. With laser excitation and the variant (b) of the fluorescence cell in *Fig. 1* deposition of photoproducts doesn't cause trouble if the two windows through which the excitation light passes are not imaged onto the entrance slit of the monochromator. The windows through which the fluorescence light passes remain clear even if such a poor solvent as perfluorohexane is used. With arc lamp excitation and variant (a) of the fluorescence cell of *Fig. 1* formation of photoproducts near that part of the capillary through which the fluorescence light passes cannot be avoided. Deposited photoproducts therefore may cause trouble either by absorption of fluorescence or by emitting a delayed luminescence.

3) Delayed fluorescence of photoproducts: Photoproducts can be classified in the same way as impurities present from the beginning. Fortunately the dominating photoproducts in general are of type (d).*E.g.* the DF. spectrum of 1,2-benzanthracene remains unchanged in spite of substantial formation of photoproducts (disappearance of about 30% of the 1,2-benzanthracene) provided the excitation wavelength is not too short (366 nm). With broad band excitation (250 to 366 nm) a different DF. spectrum is found.

The preceding discussion of difficulties arising from the presence of impurities and from the formation of photoproducts might give the impression, that the interpretation of a very weak DF. as a DF. from upper excited singlet states is an altogether uncertain matter. Indeed there are many pitfalls in the spectroscopy of molecules in the triplet state and in the investigation of the fluorescence from upper excited singlet states of polyatomic molecules. Nevertheless the following criteria allow a reliable assignment of an observed DF. spectrum to the fluorescence from upper excited singlet states:

1) The spectrum of the DF. $S_1 \rightarrow S_0$ is identical with the spectrum of the PF. $S_1 \rightarrow S_0$ - apart from a different ratio of monomer fluorescence and excimer fluorescence (*cf.* however Sect. 4.2).

2) The spectrum of the DF. is independent of excitation wavelength.

3) The spectrum of the DF. is independent of the concentration as long as fluorescence reabsorption can be neglected.

4) At low concentration of molecules in the triplet state when only a small fraction of the triplets decays by TTA, the decay of the DF. is approximately exponential. (This is not a necessary condition: In general the primary population of the three substates of T_1 by intersystem crossing from S_1 differs from thermal equilibrium population ("optical spin polarization" [23]). At low temperature attainment of thermal equilibrium population of the three substates of T_1 ("spin-lattice relaxation") may be sufficiently slow [23], and consequently the rate constants for the different TTA channels may depend on time [8]).

5) The time-dependence of different bands in the DF. spectrum is the same.

6) The spectrum of the DF. is independent of the average delay time. This is a corollary of 5) which is more easily verified than 5).

7) The spectrum of the DF. is independent of the excitation energy.

8) The spectrum of the DF. extends rather sharply to the energy of two triplets.

9) There is a mirror image relation between the bands in the DF. spectrum and the bands in the absorption spectrum. (This is not a necessary condition).

3. Results. - Corrected DF. spectra and absorption spectra of 1,2-benzanthracene, fluoranthene, pyrene, and chrysene in methylcyclohexane at −80° are shown in *Figures 2* to *5*. In the upper part of the figures spectra are shown on a logarithmic scale. 0,0-transitions to different excited singlet states in the absorption spectra and the energy of two triplets are indicated by arrows. The numbering of excited singlet states S_i $(i = 1, 2, \ldots)$ is phenomenological. In the linear plots in the lower parts of the figures additionally the difference spectra of $S_1 \rightarrow S_0$ DF. spectra and $S_1 \rightarrow S_0$ PF. spectra are shown.

3.1. *1,2-Benzanthracene.* The spectrum of the delayed luminescence of 1,2-benzanthracene *(Fig. 2)* consists of at least five different components: The phosphorescence $T_1 \rightarrow S_0$, the DF. from the lowest excimer state, the monomer DF. $S_1 \rightarrow S_0$, and the DF.'s $S_2 \rightarrow S_0$ and $S_3 \rightarrow S_0$. The 0,0-transition of the phosphorescence is at 16760 cm^{-1}. The energy 2 $E(T_{1,0})$ of two triplets (33520 cm^{-1}) is just sufficient for primary population of $S_{3,0}$ (33400 cm^{-1}) by TTA, and there is little doubt that the DF. in the spectral range from 30000 cm^{-1} to 33500 cm^{-1} is due to the DF. $S_3 \rightarrow S_0$. The first peak in the DF. spectrum at 33300 cm^{-1} is only 100 cm^{-1} red-shifted with respect to the corresponding peak in the absorption spectrum, and the second peak at 32630 cm^{-1} ($\Delta\tilde{\nu} = -670$ cm^{-1}) in the DF. spectrum is symmetric to the shoulder at 34000 cm^{-1} ($\Delta\tilde{\nu} = +600$ cm^{-1}) in the absorption spectrum. The spectrum of the DF. extends to higher energies than 2 $E(T_{1,0})$. This can be explained by TTA of molecules in vibronic states $T_{1,v}$. The

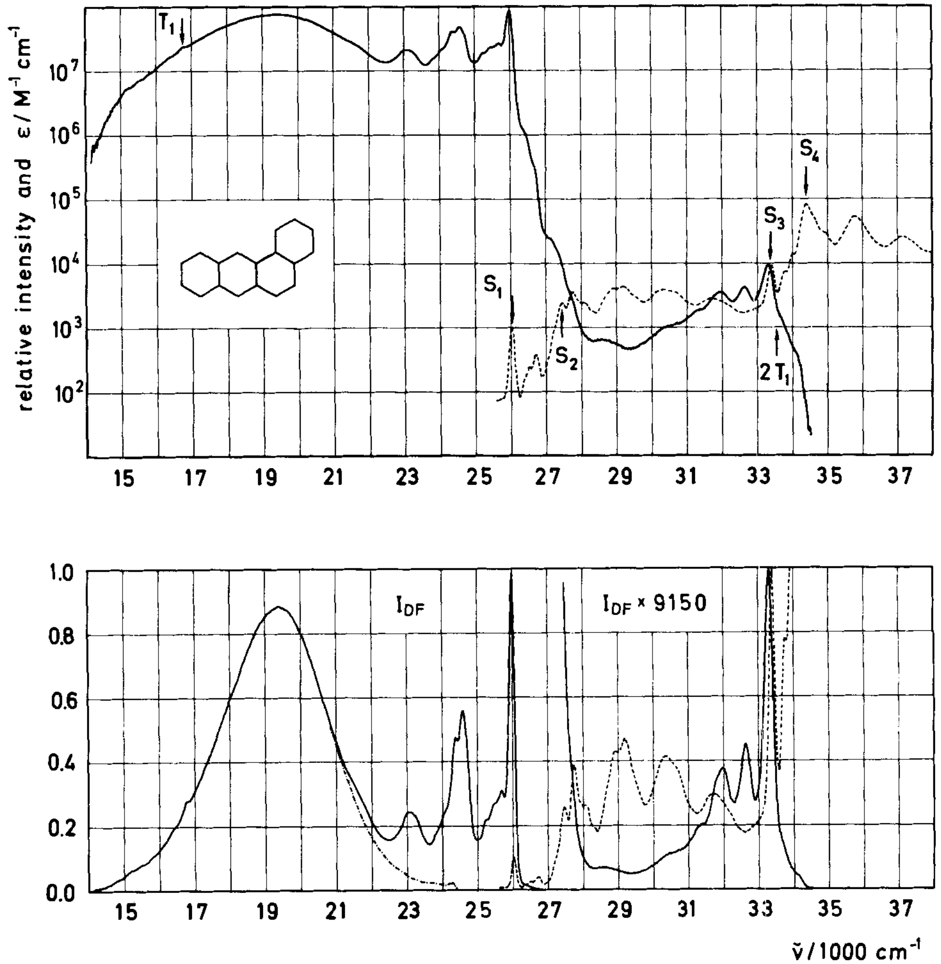

Fig. 2. *Corrected delayed luminescence* (DL.) *spectrum* (———) *and absorption spectrum* (-----) *of 1,2-benzanthracene in MCH at* $-80°$. The DL. spectrum was measured with a $5 \cdot 10^{-5}$M solution; excitation with the 365/366 nm mercury lines; spectral resolution 1.2 nm; essentially the same DL. spectrum is found with laser excitation at 351.1 nm or 363.8 nm and with a better double monochromator. In the logarithmic plot (upper part) 0,0-transitions and the energy of two triplets are indicated by arrows. In the linear plot (lower part) additionally the difference spectrum (-·-·-) of the DL. spectrum and the $S_1 \rightarrow S_0$ PF. spectrum is shown.

spectrum of the DF. must also contain a DF. $S_2 \rightarrow S_0$. However, the spectral evidence is not very conclusive. A clear distinction between hot bands of the DF. $S_1 \rightarrow S_0$ and the DF. $S_2 \rightarrow S_0$ is not possible. Perhaps the broad band at 28600 cm^{-1} is mainly due to a hot band of the DF. $S_2 \rightarrow S_0$.

3.2. *Fluoranthene.* The positions of the 0,0-transitions to S_2, S_3, S_5, and S_6 *(Fig. 3)* are taken from [24]. The spectrum of the delayed luminescence of fluoranthene is expected to consist of six components: The phosphorescence $T_1 \rightarrow S_0$, the DF. from the lowest excimer state, the monomer DF. $S_1 \rightarrow S_0$, and the DF.'s

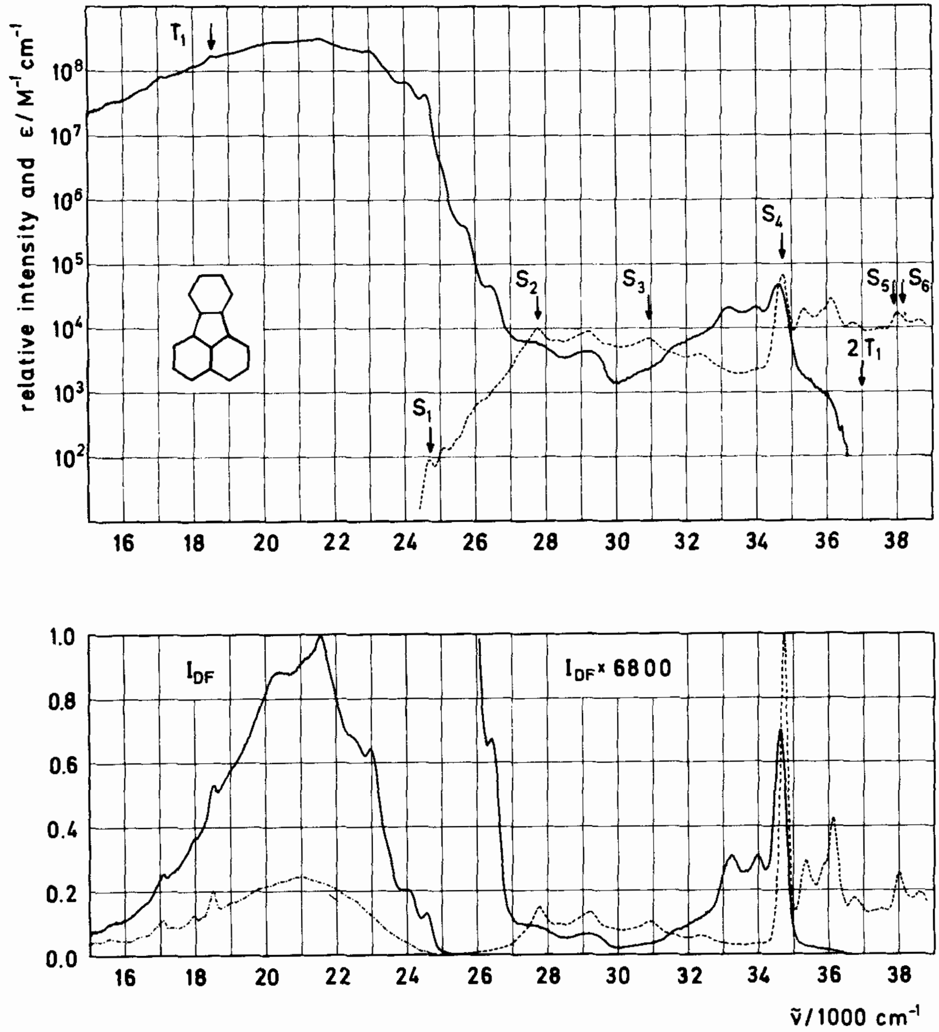

Fig. 3. *Corrected delayed luminescence* (DL.) *spectrum* (———) *and absorption spectrum* (-----) *of fluoranthene in MCH at* $-80°$. The DL. spectrum was measured with a $1.0 \cdot 10^{-5}$M solution; excitation with the 365/366 nm mercury lines; spectral resolution 1.25 nm; essentially the same DL. spectrum is found with laser excitation at 351.1 nm or 363.8 nm and with a better double monochromator. In the logarithmic plot (upper part) 0,0-transitions and the energy of two triplets are indicated by arrows. The energies of the 0,0-transitions to S_2, S_3, S_5, and S_6 are taken from [24]. In the linear plot (lower part) additionally the difference spectrum (-·--·-) of the DL. spectrum and the $S_1 \rightarrow S_0$ PF. spectrum is shown.

$S_2 \rightarrow S_0$, $S_3 \rightarrow S_0$, and $S_4 \rightarrow S_0$. The 0,0-transition of the phosphorescence is at 18500 cm^{-1}. The presence of a delayed excimer fluorescence is not obvious. However, comparison with the spectrum of the PF. $S_1 \rightarrow S_0$ shows that the delayed luminescence in the range from 15000 cm^{-1} to 25000 cm^{-1} consists of three different emissions: the phosphorescence, the monomer fluorescence $S_1 \rightarrow S_0$, and a broad structureless emission which is interpreted as a delayed excimer fluorescence. The DF. in the range from 25000 cm^{-1} to 27000 cm^{-1} must be assigned to hot bands of the DF. $S_1 \rightarrow S_0$. The broad shoulder at 27600 cm^{-1} might be due to the DF. $S_2 \rightarrow S_0$. There is no clear evidence for a DF. $S_3 \rightarrow S_0$. The DF. in the range from 31000 cm^{-1} to 35000 cm^{-1} is obviously the DF. $S_4 \rightarrow S_0$. In the first investigation of the DF. of upper excited singlet states of fluoranthene [9] additional rather sharp bands at 26350 cm^{-1} and 28200 cm^{-1} were found. These bands must have been due to impurities.

3.3. *Pyrene.* The spectrum of the delayed luminescence of pyrene *(Fig. 4)* consists of four components: The phosphorescence $T_1 \rightarrow S_0$, the DF. from the lowest excimer state, and the DF.'s $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$. The 0,0-transition of the phosphorescence is at 17000 cm^{-1}. The broad band at 29500 cm^{-1} is assigned to the DF. $S_2 \rightarrow S_0$, in accordance with the interpretation of the PF. of pyrene in the gas phase by *Geldorf et al.* [25]. The spectrum of the DF. extends up to 34000 cm^{-1}, *i.e.* the energy of two triplets. Comparison of the spectrum of the DF. with the absorption spectrum in the range from 30000 cm^{-1} to 34000 cm^{-1} suggests the assignment of the DF. in this range to hot bands of the DF. $S_2 \rightarrow S_0$. The intensity distribution of the DF. in this range is discussed in Sect. 4.3.

3.4. *Chrysene.* The spectrum of the delayed luminescence of chrysene is expected to consist of five components: The phosphorescence $T_1 \rightarrow S_0$, the DF. from the lowest excimer state, and the DF.'s $S_1 \rightarrow S_0$, $S_2 \rightarrow S_0$, and $S_3 \rightarrow S_0$. The 0,0-transition of the phosphorescence is at 20000 cm^{-1}. The phosphorescence spectrum is not shown in *Figure 5*. The presence of a delayed excimer fluorescence is not obvious. However, comparison with the PF. spectrum shows, that only 77% of the DF. in the range from 21300 cm^{-1} to 28000 cm^{-1} are delayed monomer fluorescence. It is not clear whether the weakly structured difference spectrum can be assigned mainly to delayed excimer fluorescence of chrysene, or not. If the difference spectrum represents the DF. of the excimer it should vanish at high temperature because of excimer dissociation. The vibrational structure and the rather small red-shift of the excimer spectrum with respect to the monomer spectrum would indicate that the binding energy in the excimer is not much greater than in the ground-state dimer.

The DF. in the range from 33000 cm^{-1} to 38000 cm^{-1} is assigned to the DF. $S_3 \rightarrow S_0$ because of the obvious mirror symmetry between DF. spectrum and absorption spectrum. The weak shoulder in the DF. spectrum at 31000 cm^{-1} can be assigned to the DF. $S_2 \rightarrow S_0$.

The nature of the broad DF. band at 29000 cm^{-1} is not yet clear. This band was absent in the PF. of a fresh solution of chrysene, but it was present after prolonged intense irradiation. The appearance of the broad band did not depend on excitation wavelength. If the broad band is due to a photoproduct, its DF. can be explained in different ways. The most probable photoproduct would be a photodimer $^1(M \supset M)$. The DF. of a photodimer may be due either to the photodimer being formed in its lowest excited singlet state by TTA, $^3M^* + {}^3M^* \rightarrow {}^1(M \supset M)^*$ or to mixed or homogeneous TTA, *e.g.* $^3(M \supset M)^* + {}^3M^* \rightarrow {}^1(M \supset M)^* + {}^1M$. One would expect the absorption band $S_1 \leftarrow S_0$ and the fluorescence band $S_1 \rightarrow S_0$ of the

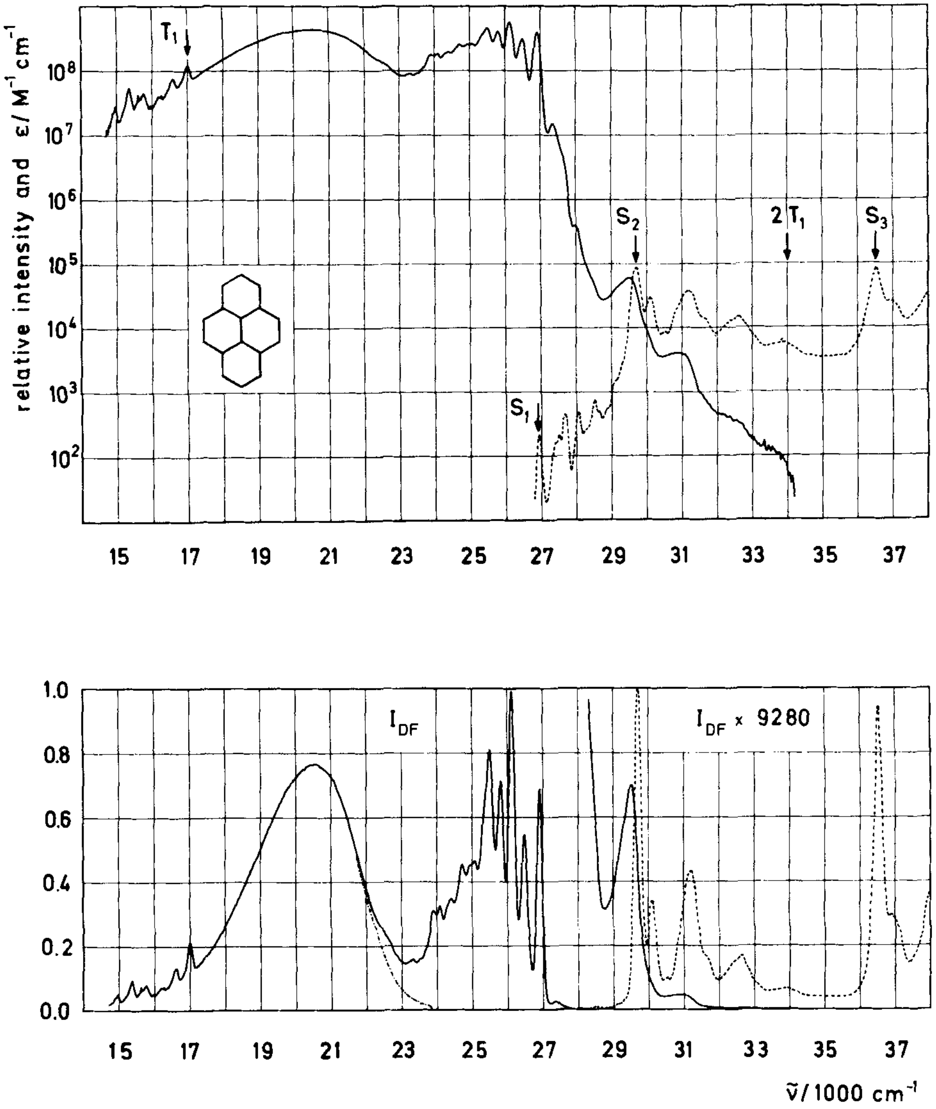

Fig. 4. *Corrected delayed luminescence* (DL.) *spectrum* (———) *and absorption spectrum* (-----) *of pyrene in MCH at* $-80°$. The DL. spectrum was measured with a $1.0 \cdot 10^{-5}$M solution; excitation with the 334 nm mercury line; spectral resolution 2.1 nm between 25000 cm^{-1} and 34000 cm^{-1} and 1.0 nm below 25000 cm^{-1}; essentially the same DL. spectrum (apart from better resolution in the region of $S_1 \rightarrow S_0$ monomer DF.) is found with laser excitation at 333.6 nm and with a better double monochromator. In the logarithmic plot (upper part) 0,0-transitions and the energy of two triplets are indicated by arrows. In the linear plot (lower part) additionally the difference spectrum (-·-·-) of the DL. spectrum and the $S_1 \rightarrow S_0$ PF. spectrum is shown. The energy difference between the onset of the difference spectrum (23800 cm^{-1}) and the 0,0-transition $S_{1,0} \rightarrow S_{0,0}$ (26900 cm^{-1}) approximately equals the excimer binding energy of pyrene in cyclohexane ($\simeq 3300$ cm^{-1}, *cf.* [3], *Table 7.4*). The onset of the difference spectrum therefore can be assigned to the 0,0-transition of the excimer fluorescence.

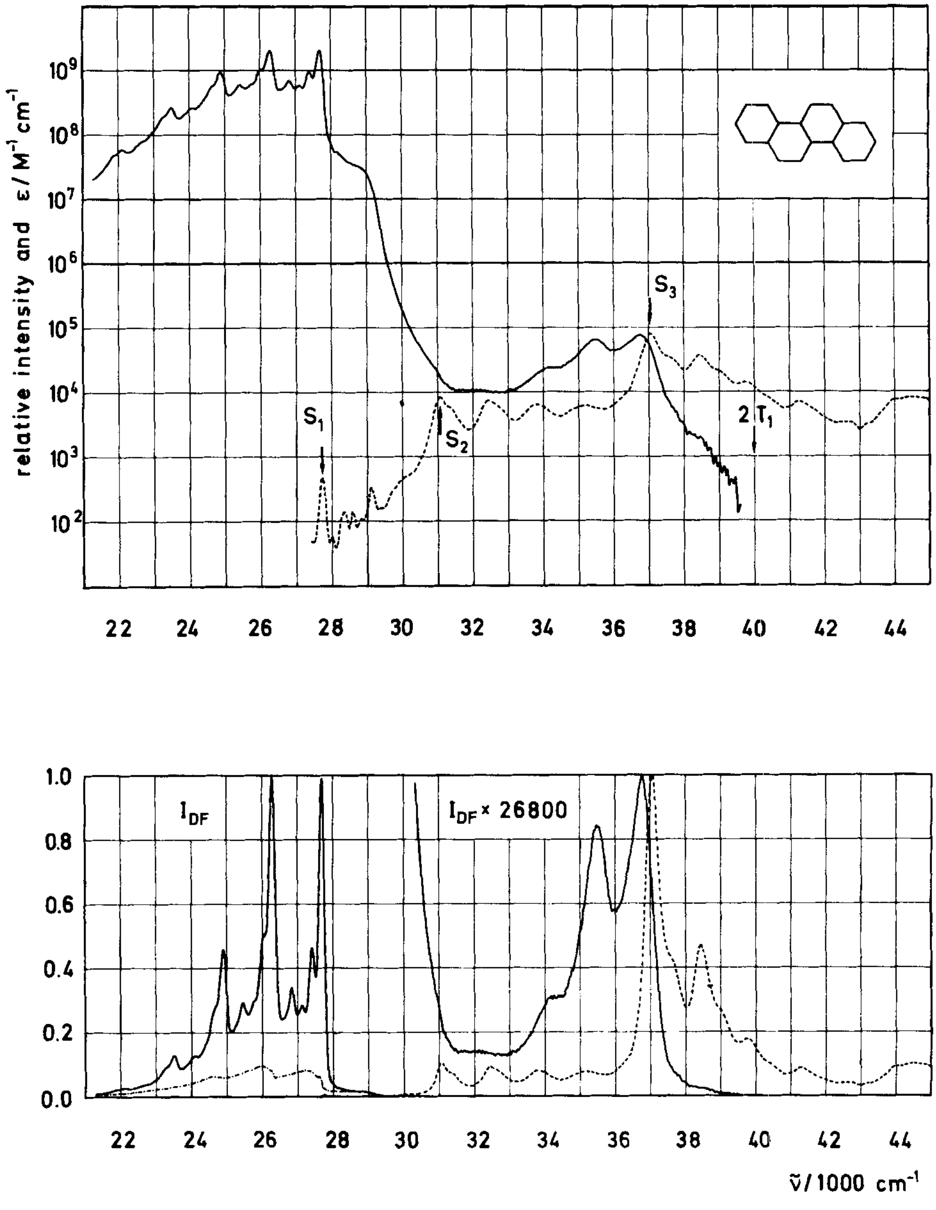

Fig. 5. *Corrected DF. spectrum* (———) *and absorption spectrum* (-----) *of chrysene in MCH at* $-80°$. The DF. spectrum was measured with a $1.0 \cdot 10^{-5}$M solution; excitation at 270 nm; spectral resolution 0.85 nm below 29000 cm^{-1} and 1.25 nm above 29000 cm^{-1}; the shoulder in the DF. spectrum at 29000 cm^{-1} was also found with laser excitation at 351.1 nm. In the logarithmic plot (upper part) 0,0-transitions and the energy of two triplets are indicated by arrows. In the linear plot (lower part) additionally the difference spectrum (-·-·-) of the DF. spectrum and the $S_1 \rightarrow S_0$ PF. spectrum is shown.

most probable photodimer to be similar to those of 5,6-dihydrochrysene (0,0-transition of $S_1 \leftarrow S_0$ at 29200 cm^{-1} [26]) - in agreement with the observed DF. spectrum.

4. Discussion. - 4.1. *Lifetimes of upper excited singlet states S_n; relative probability of primary population of S_n by TTA.* Lifetimes τ_n of upper excited singlet states S_n ($n > 1$) of large molecules in general are very short, and a direct method for the determination of τ_n does not exist. τ_n can be determined indirectly either from the quantum yield of the fluorescence $S_n \rightarrow S_0$ and the radiative lifetime τ_n^f of S_n (obtained from the absorption spectrum [27]) - if the fluorescence $S_n \rightarrow S_0$ can be measured [28] - or from the line-width of the 0,0-transition $S_{n,0} \leftarrow S_{0,0}$ [29-31]. Comparison of the lifetimes τ_n obtained by these two methods allows an estimate of the relative probability of primary population of S_n by TTA.

For determination of the lifetime τ_n of S_n by the first method the following data are available:

1) The ratio $DF._n/DF._1$ of the integrated intensities $DF._n$ and $DF._1$ of the DF.'s $S_n \rightarrow S_0$ and $S_1 \rightarrow S_0$.

2) The quantum yield ϕ_1 of the PF. $S_1 \rightarrow S_0$.

3) The radiative lifetime τ_n^f of S_n, calculated from the absorption spectrum [27].

In order to obtain from these data the lifetime τ_n of S_n several assumptions have to be made:

a) If several excited singlet states S_i ($i = 1, 2, \ldots, n$) can be populated by TTA, then there is no a priori knowledge of the relative probability P_i of primary population of S_i by TTA. The situation is more complicated than with excitation by one-photon absorption because the excess energy $2\,E(T_{1,0}) - E(S_{i,0})$ can be distributed over the two interacting molecules in different ways. Thus an additional statistical factor is coming in which is absent in one-photon excitation of isolated molecules. However, at least the spectrum of the DF. of fluoranthene strongly suggests that in this case S_4, the highest excited singlet state accessible by TTA, is preferentially populated by TTA. This is concluded from the fact that the DF.'s $S_3 \rightarrow S_0$ and $S_2 \rightarrow S_0$ are at least one order of magnitude weaker than the DF. $S_4 \rightarrow S_0$. If the steady-state concentrations of molecules in S_2, S_3, and S_4 were equal one would expect the intensity ratios $DF._2 : DF._3 : DF._4$ to roughly be the same as those of the oscillator strengths f_2 (0.17), f_3 (0.05), and f_4 (0.55) [24]. The relative steady-state concentrations of molecules in S_2, S_3, and S_4 depend on the relative probabilities P_i of primary population of S_i by TTA and on rates and pathways of internal conversions $S_i \rightsquigarrow S_1$. If the internal conversion $S_4 \rightsquigarrow S_1$ passes through S_3 and S_2 and if the rate constants of the internal conversions $S_4 \rightsquigarrow S_3$, $S_3 \rightsquigarrow S_2$, and $S_2 \rightsquigarrow S_1$ are approximately equal, the observed intensity distribution of the DF. spectrum is consistent with predominant (with respect to excited singlet states) primary population of S_4 by TTA. Incidentally also with pyrene and chrysene the highest state S_n accessible by TTA is that with the greatest oscillator strength of all accessible states, and with 1,2-benzanthracene $f_3 \simeq f_2 > f_1$. Now the assumption is made that the primary population of the highest accessible state S_n by TTA is dominant if the relation $f_n \gtrsim f_m$ ($m = 1, 2, \ldots, n-1$) holds.

b) It is assumed that internal conversion $S_n \rightarrow S_1$ is nearly quantitative. This assumption has been verified for many compounds by the independence of the quantum yield ϕ_1 of the PF. $S_1 \rightarrow S_0$ on excitation energy (*Vavilov's* rule). But there are notable exceptions such as benzene and naphthalene.

c) If a substantial fraction of the DF. $S_1 \rightarrow S_0$ is delayed excimer fluorescence, a knowledge of the quantum yield of excimer fluorescence is needed. If no data are available the quantum yield of the excimer fluorescence is assumed to equal that of the monomer fluorescence, ϕ_1. Moreover the temperature dependence of ϕ_1 is neglected.

d) With 1,2-benzanthracene a part of the absorption band $S_3 \leftarrow S_0$ is hidden under the much stronger absorption band $S_4 \leftarrow S_0$, and with pyrene a part of the DF. band $S_2 \rightarrow S_0$ is hidden under the much stronger DF. band $S_1 \rightarrow S_0$. For the calculation of the raditive lifetime τ_n^f of S_3 of 1,2-benzanthracene and of the integrated intensity $DF._2$ of the DF. $S_2 \rightarrow S_0$ of pyrene, mirror symmetry between absorption spectrum and fluorescence spectrum (with respect to a definite transition) is assumed.

e) The DF. from very short-lived upper excited singlet states S_n is always the fluorescence of pairs of interacting molecules (*cf.* Sect. 4.2). Distance and relative orientation of the two interacting molecules during the lifetime of S_n must be nearly the same as during TTA. Nevertheless it is assumed that the radiative lifetime of S_n of a pair of interacting molecules is approximately the same as that of S_n of a single molecule - as long as the interaction is sufficiently small. (If this assumption is correct the true radiative lifetime of S_1 of the α,ω-diarylalkanes and related compounds should be by a factor of 2 larger than the radiative lifetime calculated with the *Strickler-Berg* formula [27] from the absorption spectrum).

f) The rate constant of internal conversion of the state S_n of pairs of interacting molecules into lower excited singlet states is assumed to be the same as that of isolated molecules. This assumption is questionable at least in those cases where a considerable excess energy $2\,E(T_{1,0}) - E(S_{n,0})$ is available because in general the rate constant of internal conversion of S_n should increase with increasing vibrational energy of S_n.

With these assumptions and with $\tau_n \ll \tau_n^f$ the following simple formula for τ_n is obtained:

$$\tau_n \simeq \tau_n^f \Phi_1 \, DF._n / DF._1 \qquad (7)$$

Lifetimes τ_n calculated with (7) for the highest states S_n accessible by TTA. are shown in *Table 1.*

An independent estimate of the lifetime of an upper excited singlet state S_n can be based on a comparison of the line-widths of the 0,0-transitions $S_{n,0} \leftarrow S_{0,0}$ and $S_{1,0} \leftarrow S_{0,0}$ [29] [30]. If the larger line-width of $S_{n,0} \leftarrow S_{0,0}$ is completely due to homogeneous broadening by very rapid internal conversion of $S_{n,0}$ into lower excited states and if the decay of $S_{n,0}$ is exponential then the shape of the difference

Table 1. *Estimated lifetimes of the highest excited singlet states S_n accessible by TTA.* τ_n was calculated with (7), τ'_n with (8). Fluorescence quantum yields Φ_1 were taken from [3] and from [35] (for chrysene). The 0,0-transition $S_{1,0} \leftarrow S_{0,0}$ of fluoranthene is not sufficiently well separated at $-80°$; for this reason the half-width γ_1 of fluoranthene was assumed to be the same as that of pyrene..

	n	DF_n/DF_1	Φ_1	τ^f_n/s	τ_n/s	τ'_n/s	$\Delta\gamma$/cm^{-1}
1,2-Benzanthracene	3	$2.9 \cdot 10^{-5}$	0.19	$2.4 \cdot 10^{-8}$	$1.3 \cdot 10^{-13}$	$\sim 1.6 \cdot 10^{-13}$	33
Fluoranthene	4	$4.2 \cdot 10^{-5}$	0.25	$2.5 \cdot 10^{-9}$	$2.6 \cdot 10^{-14}$	$\gtrsim 5 \cdot 10^{-14}$	~ 100
Pyrene	2	$5.3 \cdot 10^{-5}$	0.65	$2.6 \cdot 10^{-9}$	$9.0 \cdot 10^{-14}$	$\gtrsim 3.8 \cdot 10^{-14}$	140
Chrysene	3	$8.3 \cdot 10^{-5}$	0.23	$1.0 \cdot 10^{-9}$	$1.9 \cdot 10^{-14}$	$\gtrsim 1.7 \cdot 10^{-14}$	314

line must be Lorentzian and the half-width $\Delta\gamma = \gamma_n - \gamma_1$ of the difference line is given by [32]:

$$\Delta\gamma = (2\pi c \tau'_n)^{-1} \tag{8}$$

with τ'_n the reciprocal rate constant of internal conversion of $S_{n,0}$ (*i.e.* in practice the lifetime of $S_{n,0}$ if $\tau'_n \ll \tau^f_n$) and c the velocity of light. Whether or not the assumption is admissible that the difference in half-width is mainly due to homogeneous broadening depends on the experimental conditions and on the particular compound. The experimental conditions are favourable if a compound is dissolved in a suitable host crystal [33] [29] with only one class of energetically equivalent sites and if the temperature is low (4 K). Under these conditions zero-phonon lines can be observed and the half-width of vibronic transitions $S_{1,v} \leftarrow S_{0,0}$ is ~ 1 cm^{-1}. The experimental situation is less favourable with *Shpolskii* matrices because of the presence of energetically inequivalent sites [30]. The compound is favourable if the transition $S_n \leftarrow S_0$ is much stronger than transitions to closely neighboured lower excited states and if 10 cm$^{-1} \lesssim \Delta\gamma \lesssim 100$ cm^{-1}, *i.e.* $\Delta\gamma$ is sufficiently large compared with γ_1 but still sufficiently small so that single vibronic transitions $S_{n,v} \leftarrow S_{0,0}$ can be distinguished [29]. For molecules in a liquid solution at a comparatively high temperature (MCH, 193 K) the situation is rather unfavourable for the evaluation of τ'_n. It cannot be taken for granted that sequence broadening and broadening due to fluctuations of environment are approximately the same for different electronic transitions. Nevertheless also for molecules in liquid solutions the comparison of band-widths should allow a crude estimate of the lifetime of very short-lived upper excited singlet states. In *Table 1* values of $\Delta\gamma$ and of τ'_n, calculated with (8), are listed.

The values of τ'_n in *Table 1* must be regarded as lower limits of the lifetimes of S_n for the following reason: It is well known that the position of electronic transitions of solute molecules depends on the solvent (more specifically on its dielectric constant and refractive index) [34]. There is a direct correlation between oscillator strength and solvent dependence of a transition. With all four compounds in *Table 1* the transition $S_n \leftarrow S_0$ is by an order of magnitude or more stronger than the transition $S_1 \leftarrow S_0$. Consequently not only the red-shift of $S_n \leftarrow S_0$ (with respect to $S_n \leftarrow S_0$ of molecules in the gas phase) will be grater than that of $S_1 \leftarrow S_0$ but also the inhomogeneous broadening due to fluctuations of the environment should be greater (this is the analogue of the vibronic transition dependence of site splittings in *Shpolskii* matrices [30]). In view of this consideration and of the assumptions (a) - (f) implied in the calculation of τ_n from DF. data, the good agreement of τ_n and τ'_n for 1,2-benzanthracene and chrysene *(Table 1)* must be considered as fortuitous. However, one may savely conclude that with all four compounds in *Table 1* primary population of S_n by TTA is one of the dominating processes in the excited singlet channel (2a).

The rather large discrepancy between τ_n and τ'_n in the case of pyrene illustrates the limits of the method. If τ_n were the true lifetime of $S_{2,0}$ and τ'_n corresponded to the true homogeneous broadening of $S_{2,0} \leftarrow S_{0,0}$, the only simple explanation of τ'_n being shorter than τ_n would be that not only in the gasphase [25] but also in solution internal conversion $S_{2,0} \rightarrow S_{1,v}$ is not completely irreversible. In order to get a more reliable estimate of the homogenous broadening of $S_{2,0} \leftarrow S_{0,0}$ of pyrene the absorption spectrum and the DF. spectrum of a $2 \cdot 10^{-6}$ molar solution of pyrene in perfluorohexane were measured at $-40°$. Solute-solvent interaction in perfluorinated alkanes is comparatively small and absorption and fluorescence spectra of solutes are very similar to the spectra of the solute molecules in the gas-phase [36] (in thermal equilibrium). In the absorption spectrum for $S_{2,0} \leftarrow S_{0,0}$ the half-width $\gamma_2 = (186 \pm 5)$ cm^{-1} was found, in the DF. spectrum for $S_{1,0} \rightarrow S_{0,0}$ the half-width $\gamma_1 = (141 \pm 5)$ cm^{-1} was found (the solubility of pyrene in perfluorohexane was too low for an accurate measurement of the absorption transition $S_{1,0} \leftarrow S_{0,0}$). With $\Delta\gamma = \gamma_2 - \gamma_1 = (45 \pm 10)$ cm^{-1} and with (8) the lifetime $\tau'_2 = 1.2 \cdot 10^{-13}$ s is obtained, in satisfactory agreement with $\tau_2 = 9 \cdot 10^{-14}$ s *(Table 1)*.

4.2. *Delayed excited dimer fluorescence.* The DF. due to TTA of molecules in solutions is always the fluorescence of pairs of interacting molecules. The strength of interaction depends on the electronic transitions involved, on the distance l and on the relative orientation of the interacting molecules [37]. If $\bar{l}_0$ is the average distance of the two molecules at the moment of TTA and if - for the moment - excimer formation is neglected then the average distance $\bar{l}$ of the molecules at the moment of emission of DF. $S_1 \rightarrow S_0$ will be

$$\bar{l} = \bar{l}_0 + (6(2D)\tau_1)^{1/2} = \bar{l}_0 + \Delta\bar{l} \qquad (9)$$

with 2D the diffusion coefficient for relative diffusion and τ_1 the lifetime of S_1. In order to illustrate the order of magnitude of the average displacement $\Delta\bar{l}$ two examples are given: With pyrene in MCH at $-80°$ one obtains $\Delta\bar{l} \simeq 2.4 \cdot 10^{-6}$ cm $=$ 240 Å ($\tau_1 \simeq 5 \cdot 10^{-7}$ s, $D \simeq 1.0 \cdot 10^{-6}$ cm^2 s^{-1} - this value is obtained with the *Stokes-Einstein* equation from the measured value of D of ^{3}pyrene* in hexane at 25.0° [20]), and with anthracene in MCH at $-80°$ one obtains $\Delta\bar{l} \simeq 2.7 \cdot 10^{-7}$ cm $=$ 27 Å ($\tau_1 \simeq 5 \cdot 10^{-9}$ s, $D \simeq 1.2 \cdot 10^{-6}$ cm^2 s^{-1} - [20]). The average displacement $\overline{\Delta l}$ can be compared with the average distance $\bar{R}$ between a molecule and its nearest neighbour for statistical distribution of solute molecules [38]:

$$\bar{R} = [(4\pi/3)\, N_L\, (10^{-3}\ l\ cm^{-3})\, c]^{-1/3} \qquad (10)$$

With the typical concentration $c = 1 \cdot 10^{-5}$ M one obtains $\bar{R} = 3.4 \cdot 10^{-6}$ cm $=$ 340 Å. Thus in general in delayed fluorescence the average distance between an excited molecule and the nearest ground-state molecule is considerably smaller than in prompt fluorescence.

The fact that the DF. is always emitted by pairs of interacting molecules manifests itself in two ways: Rather obviously in the occurrence of a delayed excimer fluorescence at arbitrarily low concentration of molecules in the electronic ground-state and less obviously in a slight difference between the spectra of the "monomer" DF. $S_1 \rightarrow S_0$ and the PF. $S_1 \rightarrow S_0$. For the determination of the excimer bands in *Figures 2* to *5* it was assumed that this difference is negligibly small. This assumption is not always justified. With perylene in MCH at $-80°$ a significant difference between DF. $S_1 \rightarrow S_0$ and PF. $S_1 \rightarrow S_0$ was found *(Fig. 6)*. In the DF. spectrum the bands are slightly broadened and slightly red-shifted. The red-shift $\Delta E \simeq 30\ \mathrm{cm}^{-1}$ can be considered as a measure of the interaction energy of the two interacting molecules in DF. ΔE should be roughly proportional to $(\tau_1^f)^{-1} r^{-3}$ where τ_1^f the radiative lifetime of S_1 and r the average distance of the interacting molecules [37]:

$$\Delta E \propto 1/(\tau_1^f\, r^3) \tag{11}$$

If the broadening and the red-shift in the DF. $S_1 \rightarrow S_0$ of perylene is indeed due to interaction of perylene molecules then with the aid of (11) the red-shift of the 0,0-transition $S_{i,0} \rightarrow S_{0,0}$ in the DF. of other compounds can predicted and

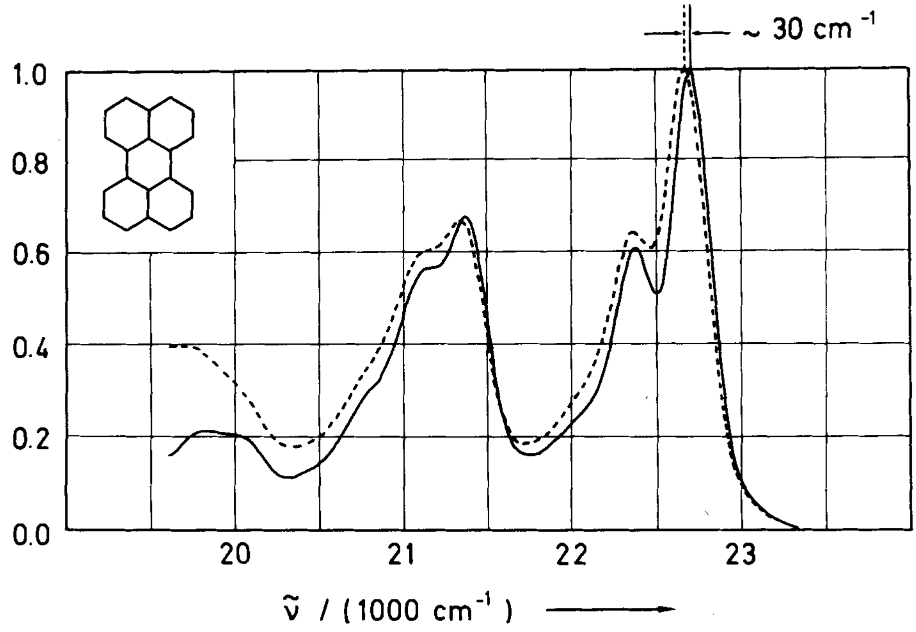

Fig. 6. *PF. spectrum* (———) *and DF. spectrum* (-----) *of perylene in MCH at* $-80°$. The solution was $2 \cdot 10^{-5}$M in perylene and $1 \cdot 10^{-4}$ in pyrene; the PF. was excited at 386 nm; the DF. was measured as sensitized DF. (excitation of pyrene at 334 nm); a glass apparatus (*Fig. 1*, variant (a)) with a capillary of 1 mm diameter was used; spectral resolution 0.5 nm.

compared with the experimentally found red-shift. This has been done for the DF. $S_1 \rightarrow S_0$ of anthracene and of pyrene and for the DF. $S_4 \rightarrow S_0$ of fluoranthene *(cf. Table 2)*.

Table 2. *Comparison of observed and predicted red-shift* ΔE *of 0,0-transitions in DF. spectra*

Compound	Perylene	Anthracene	Pyrene	Fluoranthene
Transition	$S_1 \rightarrow S_0$	$S_1 \rightarrow S_0$	$S_1 \rightarrow S_0$	$S_4 \rightarrow S_0$
Solvent	MCH	hexane	MCH	MCH
Temperature/°C	-80	-80	-80	-80
τ_i/s	$6.4 \cdot 10^{-9}$	$4.5 \cdot 10^{-9}$	$4.5 \cdot 10^{-7}$	$3 \cdot 10^{-14}$
τ_i^f/s	$6.4 \cdot 10^{-9}$	$1.6 \cdot 10^{-8}$	$6.9 \cdot 10^{-7}$	$2.5 \cdot 10^{-9}$
D/(cm^2 s^{-1})	$9 \cdot 10^{-7}$	$6 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
$(12\,D\tau_i)^{1/2}$/cm	$26 \cdot 10^{-8}$	$57 \cdot 10^{-8}$	$230 \cdot 10^{-8}$	$0.1 \cdot 10^{-8}$
$\bar{l}$/cm	$36 \cdot 10^{-8}$	$67 \cdot 10^{-8}$	$240 \cdot 10^{-8}$	$10 \cdot 10^{-8}$
$[(\tau_i^f \bar{l}^3)^{-1}]_{relat.}$	1.00	0.064	$3 \cdot 10^{-5}$	122
$(\Delta E)_{obs.}$/cm^{-1}	30 ± 6	1.5 ± 0.5	< 5	$\lesssim 100$
$(\Delta E)_{pred.}$/cm^{-1}		1.9 ± 0.4	0.001	3700 ± 800

The average distance l_0 of the interacting molecules during TTA was assumed to be 10 Å for all four compounds. For the measurement of the DF. and PF. of anthracene the experimental set-up was different from that described in Sect. 2.3. The reproducibility of the starting wavelength of the double monochromator (described in [15]) was better than ±0.005 nm, corresponding to ±0.4 cm^{-1} at 377 nm, the wavelength of the 0,0-transition of $S_1 \rightarrow S_0$ of anthracene. With anthracene predicted red-shift and observed red-shift agree within the experimental accuracy. With pyrene (and also with 1,2-benzanthracene, fluoranthene, and chrysene) the red-shift of the DF. $S_1 \rightarrow S_0$ should be much less than 1 cm^{-1}, and the observed red-shift ($\lesssim 5$ cm^{-1}) is certainly due to insufficient constancy of experimental conditions.

With fluoranthene the prediction of the red-shift of the DF. $S_4 \rightarrow S_0$ by (11) is completely wrong. This failure throws some doubt on the interpretation of the red-shift of the DF. $S_1 \rightarrow S_0$ of perylene. However, the simple relation (11) cannot be expected to apply for short distances (contact) of the two interacting molecules, and moreover during TTA the relative orientation of the interacting molecules certainly is not completely statistical. If for instance the transition moments of the two interacting molecules were perpendicular to each other the interaction energy should vanish [37]. Little seems to be known about the dependence of TTA on the relative orientation of the interacting molecules.

Excimer formation is not a necessary step in the formation of excited singlet states by TTA. This follows most directly from the decrease of the ratio DF.$_{excimer}$/DF.$_{monomer}$ with increasing solvent viscosity [39] [40]. In sufficiently fluid solutions excimer formation as a primary process in TTA cannot completely be excluded. However, the observed spectra of the DF. from upper excited singlet states indicate that primary population of upper excimer states by TTA does not occur to an appreciable extent with the compounds investigated in this paper. Possibly with naphthalene primary population of an upper excimer state by TTA does occur. The energy of two triplets of naphthalene (42600 cm^{-1}) is not sufficient for primary population of $S_3(B_{3u}^+)$ (45300 cm^{-1} in hexane) by TTA, but it should be *sufficient* for primary population of the corresponding excimer state. Indeed in the DF. spectrum of naphthalene a broad band with a maximum at about 39000 cm^{-1} was found [41], and this band has no counterpart in the absorption spectrum of naphthalene. A detailed investigation of the DF. of naphthalene is intended.

4.3. *Vibrational selection rules in TTA.* A general feature of the fluorescence from very short-lived excited states is that even in condensed phase the emitting molecules are not in thermal equilibrium with respect to their vibrational energy [29]. This follows immediately from the fact that with large molecules internal conversion $S_{n,v} \rightarrow S_{1,v'}$ ($k_{IC.} \gtrsim 10^{13}$ s^{-1} [42]) in general is much faster than intramolecular and intermolecular vibrational relaxation $S_{n,v} \rightarrow S_{n,e}$ ($k_{VR.} \lesssim 10^{12}$ s^{-1} [43]). Consequently the spectrum of the fluorescence $S_n \rightarrow S_0$ in general depends on excitation energy. The excitation energy dependence is most obvious in the hot-band region of the fluorescence $S_n \rightarrow S_0$. In the case of a DF. $S_n \rightarrow S_0$ the hot-band region is free of disturbing emissions (in contrast to PF. $S_n \rightarrow S_0$ [28]), and from the intensity distribution in the hot-band region some information on vibrational selection rules in TTA can be obtained. A particularly illustrative example is the DF. $S_2 \rightarrow S_0$ of pyrene because with pyrene the excess energy $2\,E(T_{1,0}) - E(S_{2,0}) \simeq 4300$ cm^{-1} is rather large. The following observations can be made *(cf. Fig. 4):*

(I) The spectrum of the DF. extends up to the energy $2\,E(T_{1,0})$;

(II) The DF. band at 29500 cm^{-1} is much broader than the 0,0-transition in absorption, $S_{2,0} \leftarrow S_{0,0}$;

(III) The red-shift of the DF. band at 29500 cm^{-1} with respect to $S_{2,0} \leftarrow S_{0,0}$ is greater than that of the corresponding band of 1,2-benzanthracene (with 1,2-benzanthracene $2\,E(T_{1,0}) \simeq E(S_{3,0})$);

(IV) The intensity distribution of the DF. in the range from 30000 cm^{-1} to 34000 cm^{-1} shows some similarity to the one-photon absorption spectrum of pyrene in S_0;

(V) The decrease of the DF. intensity from 30000 cm^{-1} to 34000 cm^{-1} is smaller than the decrease of the DF. intensity in the hot-band region of $S_1 \rightarrow S_0$ from 27000 cm^{-1} to 28500 cm^{-1} despite the fact that with increasing wavenumber for S_1 the absorption and therefore also the radiative rate constant for hot-band transitions increases whereas for S_2 the radiative rate constant for hot-band transitions decreases.

A qualitatively consistent interpretation of all five observations is possible on the basis of the following assumptions respectively simplifications:

a) A distinction between electronically excited molecule and ground-state molecule is meaningful;

b) In the absorption band $S_2 \leftarrow S_0$ there is one dominating progression with a vibrational quantum of about 1400 cm^{-1}. Only this one progression is taken into account. The oscillator strength f decreases within this progression approximately exponentially with

$$f(S_{2,v} \leftarrow S_{0,0}) \propto q^v \qquad (q \simeq 0.41) \qquad (12)$$

where v is the vibrational quantum number. The rate constant k^f for the radiative transition $S_{2,v} \rightarrow S_{0,v'}$ is assumed to be

$$k^f(S_{2,v} \rightarrow S_{0,v'}) \propto q^{|v-v'|}. \tag{13}$$

c) With pyrene the excess energy $2\,E(T_{1,0}) - E(S_{2,0})$ corresponds to a wavenumber difference of about 4300 cm^{-1}. It is assumed that in TTA this excess energy is distributed as vibrational energy over the two interacting molecules. The vibrational selection rules in the TTA $(T_{1,0} \ldots T_{1,0}) \rightarrow S_{2,v} \ldots S_{0,v'})$ are assumed to be same as in one-photon absorption $S_{2,v} \leftarrow S_{0,0}$. If again only one vibration is taken into account then there are four different vibronic states $S_{2,v}$ (v = 0, 1, 2, 3) which are populated by TTA with the relative probabilities $P_{2,v}$.

d) The intensity distribution in the hot-band region of the DF. $S_2 \rightarrow S_0$ depends on the steady-state relative probabilities $P'_{2,v}$. $P'_{2,v}$ may be different from $P_{2,v}$ because of vibrational relaxation and because of the dependence of internal conversion $S_{2,v} \rightarrow S_{1,v'}$ on the vibrational energy E_v. Vibrational relaxation is completely neglected. The observed intensity distribution can be approximately described by $P'_{2,v}$ depending exponentially on the vibrational energy E_v:

$$P'_{2,v} \propto r^v \qquad (v = 0, 1, 2, 3); \qquad r \simeq 0.40. \tag{14}$$

The similarity (IV) of the vibrational structures of DF. spectrum and absorption spectrum allows different interpretations. First of all (14) clearly shows that the relative population of the vibronic states $S_{2,v}$ is far from thermal equilibrium with respect to those vibrations which are active in one-photon emission. If for the moment thermal equilibrium is assumed the corresponding equilibrium temperature T_B can be calculated from (14). With a vibrational quantum of about 1400 cm^{-1} one obtains

$$P'_{2,v} \propto r^v = P'_{2,0} \cdot \exp[-(1400\ \mathrm{cm}^{-1})v/(k_B T_B])) \tag{15}$$

with k_B the *Boltzmann* constant. With $r \simeq 0.40$ one obtains $k_B T_B \simeq 1500$ cm^{-1} or $T_B \simeq 2200$ K. The actual temperature of the sample was 193 K. Thus indeed the relative population of the vibronic states $S_{2,v}$ is far from thermal equilibrium. The similarity (IV) of the vibrational structures of DF. spectrum and absorption spectrum may be incidental if in TTA totally symmetric vibrations are preferred. The similarity of the vibrational structures would be not incidental if a correlation would exist between the probability $P_{2,v}$ of primary population of $S_{2,v}$ by TTA and the vibronic oscillator strength of the one-photon transition $S_{2,v} \leftarrow S_{0,0}$. Comparison of (12) and (14) suggests that such a correlation exists. It is rather improbable that the decrease of $P'_{2,v}$, (14), with increasing vibrational energy is completely due to an increase of the rate constant of internal conversion $S_{2,v} \rightsquigarrow S_{1,v'}$.

The observations (II) and (III) (see p. 34) are a simple consequence of the fact that the DF. $S_2 \rightarrow S_0$ is emitted from different vibronic states $S_{2,v}$. Several v, v-transitions $S_{2,v} \rightarrow S_{0,v}$ (v = 0, 1, 2, 3) in DF. correspond to the 0,0-transition

$S_{2,0} \leftarrow S_{0,0}$ in absorption. Thus the band broadening (II) and the red-shift (III) represent an unusual case of sequence broadening.

4.4. *Open questions.* The DF. from upper excited singlet states has two different aspects: It is an information on the primary process of TTA and it is of interest as a fluorescence which cannot be measured easily in any other way. With respect to both aspects there are still many open questions. Some of them will be discussed in this last section.

It has been argued that the interpretation of a DF. as a DF. $S_2 \rightarrow S_0$ may be doubtful with compounds such as pyrene or naphthalene where no mirror symmetry between absorption and fluorescence can be found because of the proximity of S_2 and S_1. Therefore it may be appropriate to mention additional performed or possible experiments which can corroborate the assignment $S_2 \rightarrow S_0$ of a DF.

a) The intensity distribution of the hot-band DF. $S_1 \rightarrow S_0$ approximately corresponds to thermal equilibrium with respect to the relative population of vibronic states $S_{1,v}$ (*cf.* Sect. 4.3). For this reason at lower temperature a larger fraction of the total $S_2 \rightarrow S_0$ DF. band will be seen. Conversely, in agreement with this consideration at $-10°$ the DF. $S_2 \rightarrow S_0$ of pyrene manifests itself only as a shoulder in the DF. spectrum [41].

b) The energy gap between S_1 and S_2 depends on the solvent. If $S_1 \leftarrow S_0$ is a weak transition and $S_2 \leftarrow S_0$ a strong transition as with pyrene and naphthalene, the energy gap increases with decreasing refractive index of the solvent. Thus with pyrene in perfluorohexane at $-40°$ the maximum of the DF. $S_2 \rightarrow S_0$ corresponding to the absorption maximum at 31200 cm^{-1} in *Figure 4* is seen as a distinct shoulder in the DF. spectrum [44], and with naphthalene at $-80°$ the DF. $S_2 \rightarrow S_0$ manifests itself in MCH only as a shoulder, but in perfluorohexane as a distinct maximum.

c) The relative intensity of the DF. $S_2 \rightarrow S_0$ with respect to the DF. $S_1 \rightarrow S_0$ can be enhanced by selective quenching of the DF. $S_1 \rightarrow S_0$. A suitable quencher for pyrene is triethylamine (TEA). S_1 of pyrene is quenched by TEA, but T_1 is not [45]. The DF. spectrum of pyrene in TEA at $-80°$ in the region of the DF. $S_2 \rightarrow S_0$ between 29000 cm^{-1} and 34000 cm^{-1} is essentially identical with the DF. spectrum of pyrene in MCH [44]. This indicates that during the short lifetime of S_2 exciplex formation does not take place. However, the intensity ratio DF.$_1$ (26900 cm^{-1})/DF.$_2$ (29500 cm^{-1}) is for MCH 6300, but for TEA only 30, and the maximum of the DF. $S_2 \rightarrow S_0$ corresponding to the absorption maximum at 31200 cm^{-1} is seen as a distinct shoulder in the DF. spectrum.

d) The intensity ratio DF.$_1$/DF.$_2$ of a compound M can be reduced by population of $S_2(M)$ by mixed TTA with a suitable compound Q: $T_1(M) + T_1(Q) \rightarrow S_2(M) + S_0(Q)$. A suitable compound Q would be an "impurity" of type (a) (*cf.* Sect. 2.5) with $E(^3Q^*) < E(^3M^*)$ and $E(^1Q^*) < E(M^*)$. The absorption of Q in the region of the DF. $S_2 \rightarrow S_0$ of M should be weak. The total DF. spectrum would consist of three components corresponding to the TTA's $T_1(M) + T_1(M)$, $T_1(M) + T_1(Q)$, and $T_1(Q) + T_1(Q)$. The first and the third component can be measured separately, so that by subtraction of these components in principle a DF. spectrum can be obtained which is completely due to mixed TTA. Each of the three spectra should extend to the sum of the energies of the respective triplets. Therefore at least subtraction of the first spectrum is possible without difficulty because there is a spectral region in which the DF. is completely due to homogenous TTA $T_1(M)+T_1(M)$. In the DF. spectrum due to mixed TTA the DF. $S_1 \rightarrow S_0$ of M is partially quenched by energy transfer $S_1(M)+S_0(Q) \rightarrow S_0(M)+S_1(Q)$. An experiment with M = pyrene and Q = perylene failed. A DF. $S_2 \rightarrow S_0$ of pyrene due to mixed TTA could not be detected. Possibly the literature value 12600 cm^{-1} for the triplet energy of perylene [46] is too high [47], and consequently in mixed TTA the energy is not sufficient for primary population of S_2 of pyrene.

According to the discussion in Sect. 4.2 and 4.3 the relative broadening of DF. bands $S_n \rightarrow S_0$ (compared with the corresponding absorption bands $S_n \leftarrow S_0$) should be due to the DF. $S_n \rightarrow S_0$ being emitted by pairs of interacting and vibrationally excited molecules. Both broadening factors can be greatly reduced if the state S_n is populated by mixed TTA. Indeed the main aim of the unsuccessful experiment mentioned above was to find out whether the vibrational structure of the DF. $S_2 \rightarrow S_0$ of pyrene is as well resolved as in the absorption band $S_2 \leftarrow S_0$ when in mixed TTA no excess energy is available and the exciton interaction is weak. For the investigation of the DF. $S_2 \rightarrow S_0$ of pyrene a suitable compound Q for mixed TTA has not yet been found. With respect to the DF. $S_4 \rightarrow S_0$ of fluoranthene pyrene is a suitable partner for mixed TTA. In the DF. spectrum due to mixed TTA of ^{3}(fluoranthene)* and ^{3}(pyrene)* the width of the first band of the DF. $S_4 \rightarrow S_0$ at 34700 cm^{-1} is smaller than in the DF. spectrum due to homogeneous TTA [44].

Another aspect of mixed TTA is the possibility to populate excited singlet states which cannot be populated by homogeneous TTA [48] [49]. *E.g.* by mixed TTA with ^{3}(acetophenone)* it should be possible to populate $S_2(B_{3u}^+)$ of anthracene, $S_3(B_{3u}^+)$ of naphthalene and of tetracene, and S_4 of pyrene, and to measure the fluorescence emitted from these states. A fluorescence from the same states will be observed with consecutive two-photon excitation $S_n \leftarrow S_1 \leftarrow S_0$ [15]. Comparison of the fluorescence spectra obtained with both methods will allow to find out to what extent the fluorescence from upper states depends on the way of excitation. The DF. spectra of 1,2-benzanthracene, fluoranthene, and chrysene show that in general only the DF. $S_1 \rightarrow S_0$ and the DF. from the highest excited singlet state accessible by TTA, $S_n \rightarrow S_0$, can be identified with certainty. With respect to the intermediate states S_k ($k = 2, \ldots, n-1$) there are two obvious questions. One would like to know the spectra of the fluorescences $S_k \rightarrow S_0$ and the relative probabilities P_k of primary population of S_k by TTA. With respect to the first question again mixed TTA should be a useful artifice because in mixed TTA a compound Q with a triplet energy can be chosen which is just sufficient for primary population of $S_k(M)$ but not of any higher states. With respect to the second question a comparison of the magnetic field dependence of the DF.'s $S_1 \rightarrow S_0$ and $S_n \rightarrow S_0$ should give some information on relative primary population probabilities. It is well known that the DF. of molecular crystals [8] and of molecules in solutions [50-52] is changed by an applied magnetic field. Theoretical explanations of the magnetic field dependence of the DF. up to now have taken into account only the spin functions of the interacting molecules [8] [52]. This simplification may be justified as long as only one excited singlet state is primarily populated by TTA. If several excited singlet states are primarily populated by TTA with comparable relative probabilities, different DF.'s may exhibit different magnetic field dependences for the following reason: The rate constant for a definite TTA channel $T_1 + T_1 \rightarrow S_i + S_0$ in general will depend on distance and relative orientation of the interacting molecules. The average relative orientation should depend on the state S_i. On the other hand it is known that the magnetic field effect strongly depends on relative orientation of the interacting molecules and the magnetic field [8] [52]. Consequently if different DF.'s can be observed which are not due to the same TTA channel, they should exhibit in general different magnetic field dependences. Up to now only the DF. of 1,2-benzanthracene has been investigated in this respect [41]. In MCH at $-80°$ the DF.'s $S_3 \rightarrow S_0$ and $S_1 \rightarrow S_0$ showed the same magnetic field dependence (up to 4.5 kG and with an accuracy of $\pm 0.2\%$). This negative result is in accordance with the assumption made in Sect. 4.1 that primarily S_3 is predominantly populated by TTA, but of course it does not prove the correctness of this assumption. There is a clear need of a theory which predicts the relative probabilities for primary population of different excited singlet states by TTA and the magnetic field dependences of the respective DF.'s.

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Note added in proof:

References [1], [4], [5], [6], and [7] concern papers in which for the first time the respective DF.'s were explained by TTA. The first observation of a DF. of an aromatic hydrocarbon was made by *P.P. Dikun* (Zh. Eksperim. i Teor. Fiz. *20,* 193 (1950)). The first explanation of this DF. by a process involving *two* molecules of the aromatic hydrocarbon was proposed by *R. Williams* (J. chem. Phys. *28,* 577 (1958)). The first explanation of a DF. (of concentrated solid solutions of naphthalene) by TTA was given by *S. Czarnecki* (Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron. Phys. *9,* 561 (1961)).

REFERENCES

[1] *C.A. Parker & C. G. Hatchard,* Proc. chem. Soc. *1962,* 147.
[2] *C.A. Parker,* 'Photoluminescence of solutions', Elsevier Publ. Corp., Amsterdam 1968.
[3] *J.B. Birks,* 'Photophysics of aromatic molecules', Wiley-Interscience, London 1970, Chapter 8.
[4] *B. Stevens, M.S. Walker & E. Hutton,* Proc. chem. Soc. *1963,* 62.
[5] *H. Sternlicht, G.C. Nieman & G.W. Robinson,* J. chem. Physics *38,* 1326 (1963).
[6] *R.G. Kepler, J.C. Caris, P. Avakian & E. Abramson,* Phys. Rev. Letters *10,* 400 (1963).
[7] *R.F. Cozzens & R.B. Fox,* J. chem. Physics *50,* 1532 (1969).
[8] *R.E. Merrifield,* Pure appl. Chemistry *27,* 481 (1971).
[9] *B. Nickel,* Chem. Phys. Letters *27,* 84 (1974).
[10] *L. Peter & G. Vaubel,* Chem. Phys. Letters *21,* 158 (1973).
[11] *L.M. Jackman,* 'Hydrogenation-dehydrogenation reactions', Adv. org. Chemistry *2,* 329 (1960).
[12] *L.H. Klemm, D.R. McCoy & D.R. Olson,* J. heterocycl. Chemistry *7,* 1347 (1970).
[13] *M. Kasha,* J. opt. Soc. Am. *38,* 929 (1948).
[14] *U. Lachmann,* unpublished result.
[15] *B. Nickel & G. Roden,* Ber. Bunsenges. phys. Chem. *81,* 281 (1977).

[16] *G.J. Sloan*, 'Definition and attainment of high purity of organic compounds' in 'Physics and chemistry of the organic solid state', D. Fox, M.M. Labes and A. Weisberger (editors), Vol. 1, 179 (1963), Interscience Publishers.

[17] *L.M. Peter & G. Vaubel*, Z. Naturforsch. *29a*, 183 (1974).

[18] *D.L. Philen & R.M. Hedges*, Chem. Physics Letters *43*, 358 (1976).

[19] *H. Labhart & W. Heinzelmann*, 'Triplet-triplet absorption spectra of organic molecules' in 'Organic molecular photophysics', J.B. Birks (editor), Vol. 1, 297 (1973), Wiley-Interscience.

[20] *E.G. Meyer*, 'Diffusionskoeffizienten von Molekülen im Triplettzustand', Dissertation Göttingen 1977.

[21] a) *H. Schildknecht*, «Zonenschmelzen», Verlag Chemie, Weinheim 1964; b) *W.G. Pfann*, 'Zonen Melting', J. Wiley, New York 1966.

[22] *D. Fischer*, «Zonenschmelzen von Aromaten», Dissertation Stuttgart 1970; *D. Fischer*, Math. Res. Bull. *8*, 385 (1973); *D. Fischer*, J. appl. Physics *44*, 1977 (1973).

[23] *K.H. Hausser & H.C. Wolf*, 'Optical spin polarization in molecular crystals', Adv. in magn. Res. *8*, 85 (1976).

[24] *J. Kolc, E.W. Thulstrup & J. Michl*, J. Am. chem. Soc. *96*, 7188 (1974).

[25] *P.A. Geldof, R.P.H. Rettschnick & G.J. Hoytink*, Chem. Physics Letters *4*, 59 (1969).

[26] DMS UV Atlas of Organic Compounds, Butterworths, London, and Verlag Chemie, Weinheim, 1966, E1/43.

[27] *S.J. Strickler & R.A. Berg*, J. chem. Physics *37*, 814 (1962).

[28] *F. Hirayama, T.A. Gregory & S. Lipsky*, J. chem. Phys. *58*, 4696 (1973).

[29] *R.M. Hochstrasser & C. Marzzacco*, J. chem. Physics *49*, 971 (1968).

[30] *J.L. Richards & S.A. Rice*, Chem. Physics Letters *9*, 444 (1971).

[31] *G. Fischer*, 'Spectroscopic implications of line broadening in large molecules', Topics in Current Chemistry *66*, 116 (1976).

[32] *W. Kauzmann*, 'Quantum chemistry', Academic Press, New York 1957, page 566.

[33] *D.S. McClure*, J. chem. Physics *22*, 1668 (1954).

[34] *N. Mataga & T. Kubota*, 'Molecular interactions and electronic spectra', Dekker, New York 1970, Chapter 8; ref. [3], Chapter 4.12.

[35] *N. Kanamaru, H.R. Bhattacharjee & E.C. Lim*, Chem. Physics Letters *26*, 174 (1974).

[36] *C.W. Lawson, F. Hirayama & S. Lipsky*, J. chem. Physics *51*, 1590 (1969).

[37] *E.G. McRae & M. Kasha*, 'The molecular exciton model' in 'Physical processes in radiation biology', L. Augenstein, R. Mason and B. Rosenberg (editors), Aademic Press, New York 1964, page 23.

[38] *Th. Förster*, Z. Elektrochem. *53*, 93 (1949).

[39] *D. Wyrsch & H. Labhart*, Chem. Physics Letters *12*, 373 (1971).

[40] *H. Labhart & D. Wyrsch*, Chem. Physics Letters *12*, 378 (1971).

[41] *B. Nickel* (unpublished).

[42] *M. Kasha*, Disc. Faraday Soc. *9*, 14 (1950).

[43] *A. Laubereau, A. Seilmeier & W. Kaiser*, Chem. Physics Letters *36*, 232 (1975).

[44] *B. Nickel & G. Roden* (unpublished).

[45] *D. Rehm & A. Weller*, private communication.

[46] Ref. [3], Table 5.4.

[47] *H. Bernhard & J.-L. Metzger* (Physikalisch-Chemisches Institut der Universität Zürich, Zürich, Switzerland), private communication; according to these authors the 0,0-transition of the phosphorescence of perylene is at about 12400 cm^{-1}.

[48] *C.A. Parker*, Proc. Roy. Soc. (London), Ser. A*276*, 125 (1963).

[49] *C.A. Parker*, Ber. Bunsenges. phys. Chem. *73*, 764 (1969).

[50] *D. Wyrsch & H. Labhart*, Chem. Physics Letters *8*, 217 (1971).

[51] *J. Spichtig, H. Bulska & H. Labhart*, Chem. Physics *15*, 279 (1976).

[52] *K. Lendi, P. Gerber & H. Labhart*, Chem. Physics *18*, 449 (1976).