Forschung, Wissenschaft

Total Luminescence Spectroscopy*

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Abstract

Total Luminescence Spectroscopy (TLS) is a method used to characterize molecules on the basis of their excitation and emission spectra. The data obtained from TLS, a 2D-spectrum, may be represented as intensity values over the excitation-emission plane. The method has, in the past, been mainly applied in the quantitative and qualitative analysis of mixtures containing luminescent molecules.

In this paper, these standard applications are reviewed. In addition, innovative applications of TLS in the field of Photophysical Chemistry are presented.

1.0 Introduction

Almost all standard luminescent applications may be easily understood with the help of a *Jablonski* diagram (fig. 1). When the molecule is excited above the S_1 level, very rapid internal conversion ensures that the molecule relaxes to the S_1 level. This level typically has a lifetime in the order of some nanoseconds and may radiatively deactivate ($S_1 \rightarrow S_0$) giving rise to fluorescence. The frequently observed excitation wavelength independence of the fluorescence spectrum may be understood with this simple model.

Intersystem crossing from S_1 may lead to a population of the triplet manifold. Again internal conversion ensures that the molecules relax to the T_1 state. Radiative deactivation of the T_1 state is called phosphorescence, and has a lifetime from milliseconds to some seconds. Thus, the phosphorescence spectrum is also generally excitation wavelength independent.

Conventional analytical applications of luminescence spectroscopy rely on these facts. Luminescent methods have the advantage that they are both highly sensitive and specific. This allows the detection of very low concentrations of luminescent molecules. In the regime of low optical densities, excluding energy transfer, the luminescent intensitiy is proportional to concentration. With the help of internal or external standards one can determine the absolute concentration of a known species in a sample. This is certainly one of the most widely used features of analytical luminescence spectroscopy.

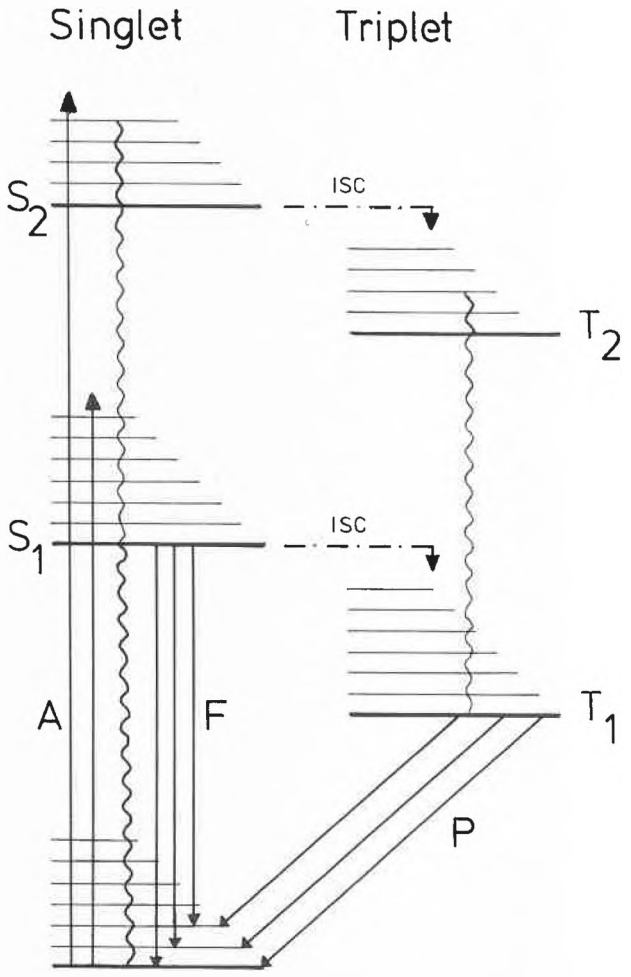

Fig. 1: Jablonski energy level diagram for an idealized molecule

The characteristics of the 2D-spectrum of a single molecular species may be seen in fig. 2. In this case the 2D-spectra of the molecule may be represented by the product of the emission and excitation spectra line shapes.

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$I(\tilde{\nu}_{em}, \tilde{\nu}_{ex}) = k * E(\tilde{\nu}_{em}) * A(\tilde{\nu}_{ex})$

where $E(\tilde{\nu}_{em})$ = shape function of the emission spectrum
$A(\tilde{\nu}_{ex})$ = shape function of the excitation spectrum
and k = a scaling constant

This product results in the characteristic pattern of the contour plot; all the local minima and maxima lie on a rectangular grid.

Fig. 3 shows a contour plot of a solution containing six polyaromatic hydrocarbons (PAHs). This spectrum may be analysed in terms of the individual subspectra, viz:

$$I_{total}(\tilde{\nu}_{em}, \tilde{\nu}_{ex}) = \sum_i k_i * E_i(\tilde{\nu}_{em}) * A_i(\tilde{\nu}_{ex})$$

where the subscript i refers to the ith component and $1 \leqslant i \leqslant 6$

The characteristic rectangular grid pattern of the subspectra is clearly apparent in local segments, where one of the compounds dominates.
Most of the literature dealing with TLS is concerned with the quantitative analysis of such 2D-mixture-spectra. Other aspects related to analytical applications of TLS may be found in [1-5].
In this work we also present some new applications of Total Luminescence Spectroscopy (TLS) to the field of Photophysical Chemistry. Excitation dependent emission spectra have been observed some for chemically pure compounds. The resulting 2D-spectra cannot be represented as the simple product of the excitation and emission shape functions. Because of the interdependence of the emission and excitation spectra individual emission and/or excitation spectra are difficult to interprete. A 2D-spectra provides all the necessary information simultaneously and greatly aids the analysis. We apply TLS to systems where the excitation emission dependencies may be due to:
(1) Edge Excitation Red Shift (EERS)
(2) Dual Phosphorescence
(3) Multisite Shpolskii-Spectra
(4) Energy-Selection Spectra

2.0 Experimental Techniques

2.1. Data acquisition

Weber's first 2D-spectra consisted of 3×3 or 4×4 intensity matrices, with indices λ_{ex} and λ_{em}. These spectra were obtained by a series of individual measurements after manually setting the monochromators [6]. Since then, various techniques for recording more detailed 2D-spectra consisting of up to 6×10^4 points have been developed.
Some of these instruments, including those commercially available [7], are based on conventional lumi-

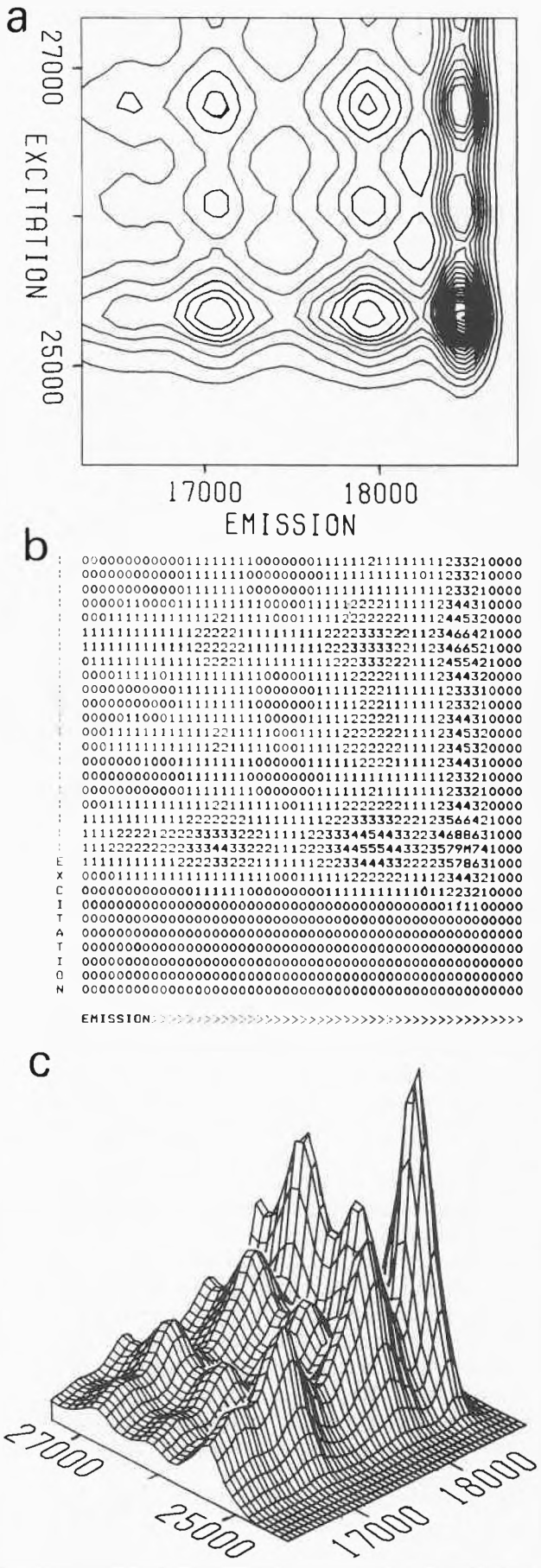

Fig. 2: The 2D-phosphorescence spectrum of dibenzo[a,c]phenazine in ethanol at 77K in different representations: (a) contour plot, (b) excitation-emission matrix (EEM), (c) isometric projection.

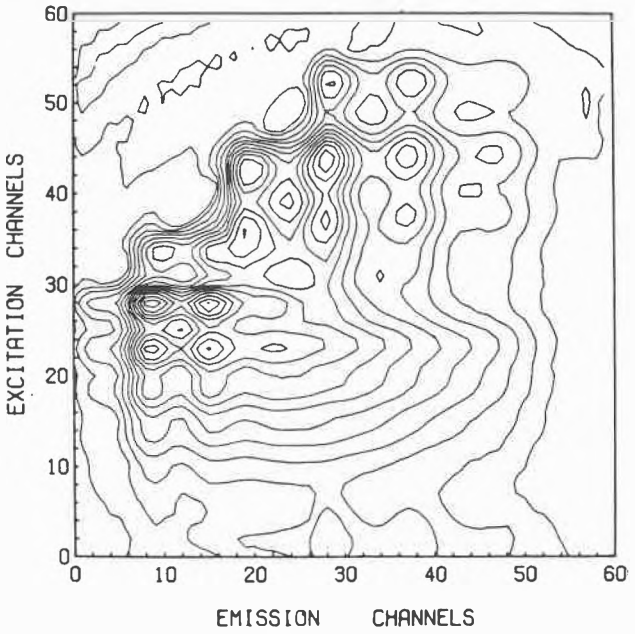

Fig. 3: Contour plot of the 2D-spectrum of a sample containing six polynuclear aromatic hydrocarbons: perylene, fluoranthene, tetracene, dimethyl-anthracene, chrysene and anthracene (from [42]).

nescence spetrometers. In the system of *Schachter* and *Haenni* [8], the 2D-spectrum is obtained from a series of synchronous scans (vide infra) with increasing wavelength differences $\Delta\lambda$. *Rho* and *Stuart* [9] and *O'Haver* and *Green* [10] developed automatic hardware controlled spectrometers that allow the generation of contour plots (cf.2.2) by sequentially scanning a series of emission spectra with different excitation wavelengths. *Haugen* et. al [11] used the sequential scan principle for the data collection in their computer controlled spectrometer, which allows the completely automatic recording and data storage of the entire 2D-spectrum.

A computer controlled high resolution spectrometer with a photon counting detector for measurements of low temperature spectra has been described by *Suter* [12]. This is perhaps one of the most versatile spectrometers used in TLS. It consists of two high resolution emission and excitation monochromators (Spex 1402), a 2.5kW Xe excitation lamp, and a RCA 31034 photomultiplier in photon counting mode, as the detector. Both monochromators are controlled directly by a DEC LSI 11/23 computer which allows them to be positioned anywhere in the $\tilde{\nu}_{ex}\cdot\tilde{\nu}_{em}$-plane. The measurements consists of counting the photons emitted during a fixed interval. With this spectrometer, a TLS experiment is performed by measuring a series of emission spectra with successive excitation frequencies. A shutter, also under computer control, protects the detector, should the monochromators cross or come within a safetey limit. This spectrometer has three channels that may be used concurrently to monitor the:

(a) fluorescence intensity
(b) sum of the phosphorescence and fluorescence intensities
(c) excitation intensity using a quantum counter.

Thus corrected phosphorescence and fluorescence spectra may be easily obtained.

The other main type of 2D-spectrometer described in the literature operates with crossed polychromators: The sample is irradiated along its vertical axis with light of varying wavelengths produced by the excitation polychromator (fig. 4). The intensity distribution of the emission along the vertical axis thus represents the excitation spectrum of the sample. The emission is focussed on the entrance slit of the emission polychromator, which disperses the light in horizontal direction. Hence, the spectral distribution of the emission coming from different vertical positions, i.e. from different excitation wavelengths, may be observed along the horizontal axis of the quadratic exit window of the emission polychromator.

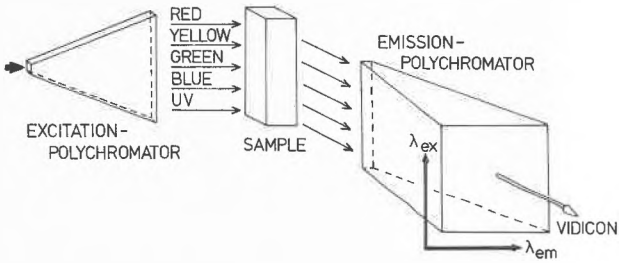

Fig. 4: A 2D-spectrometer with crossed polychromators (schematic). The emission polychromator is oriented perpendicular to the excitation polychromator (after [13]).

Using image intensifiers and a video camera, *Warner* et. al [13] have developed a system that allows the recording of 241 emission spectra with different excitation wavelengths in less than 17ms. A computer controlled version of this instrument with accumulation ans smoothing facilities has been described by *Johnson* et. al [14, 15]. A similar set up with a diode array detector has been applied by *Hornig* [16].

2.2. Data representation

2D-spectra usually are plotted as contour maps (fig. 2a) [2, 3]. In addition to the direct method of *Rho* and *Stuart* [9], these plots may easily be obtained from the intensity matrix stored in a computer using standard software. (For a sample program see [17]). Choosing different contour values may be helpful in the visual analysis of 2D-spectra [2]. In many cases, a logarithmic intensity scale yields a more detailed picture of the spectrum than the usual linear scale.

Matrix representations of the Excitation Emission Matrix (EEM) with dots of different brightness are less common [14, 15, 18]. Symbol matrices (fig. 2b) may be generated very rapidly on any printing terminal without any complicated plot routines [12]. The method, however, is limited by the number of charac-

ters per line of the printer and allows no scaling of the two axis.

Three dimensional representations in isometric projection (fig. 2c) are obtained as a real time display in the video fluorimeter of *Warner* et al. [13]. Such plots may be generated with a computer [19]. Compared with contour maps, central perspective projections are considerably less valuable in the analysis of the 2D-spectrum since practically no quantitative information (e.g. peak positions) can be read from them directly. Nevertheless, they may serve as a helpful supplement giving a good overview of the whole 2D-spectrum. Three dimensional representations have also been in the discussion of and to qualitatively compare data analysis procedures for 2D-spectra [20, 21].

2.3. Data Analysis

In many applications, TLS was used as a fingerprint method, especially for complicated multicomponent samples; e.g. for oil in water [22, 23] or for biological material [24]. *Giering* analysed the 2D-spectra of mixtures by comparison with the spectra of the pure components and visual symmetry considerations [3].

The pioneering work of *Weber* [6] included the basis for a mathematical treatment of 2D-spectra in analytical chemistry: The rank of the EEM was used to determine the number of emitting species in the solution.

Giering and *Hornig* [25] suggested a method for the calculation of the concentration of N known components in a mixture by solving a system of N linear equations of the form

$$I_i(\lambda_{em}, \lambda_{ex}) = \sum_{j=1}^{N} c_j * S_i(\lambda_{em}, \lambda_{ex})$$

where $i = 1,N$

and S_i = normalized luminescence intensities of the individual components

The 2D-spectra are used in this method to select the spectral points that lead to the simplest equations, i.e. those points where spectral overlap is minimal.

Least sqaures procedures have been proposed by *Warner* et. al [26] and by *Sternberg* et. al [27]. By the method or rank annihilation introduced by *Ho* et. al [28, 29], the concentration of known components in a mixture may be calculated even in the presence of unknown components.

The «eigenanalysis-method» of *Warner* et. al [20] enables the calculation of unknown spectra in a two-component mixture under certain conditions. The authors list the estimated ambiguities in the calculated spectra of the components as a function of the spectral overlap.

In cases where it is possible to change the relative contribution of the individual emitting species in a mixture of completely unknown components, *Fogarty* and *Warner* [21] have shown that the spectra of the pure components can be obtained by the «ratio method». Such concentration changes may be achieved for example by chemical extraction or by the addition of a quencher to the solution.

The interfacing of modern spectrometers to digital computers greatly simplifies the data treatment that is usually necessary to prepare the data for an analysis: Various corrections (e.g. for the intensity profiles of the excitation light sources, the transmittance of optical components in the set up and the sensitivity curve of the detectors) may be carried out, as well as background subtraction, data smoothing, and differentiation [11].

2.4. Related 2D-Methods

The data analysis procedures given above may also be used in other analytical spectrofluorimetric methods in which the luminescence intensity is measured as a function of two parameters; e.g. in the analysis of:

- time resolved spectra: $I_{fl} = I_{fl}(\lambda_{em},t)$ (*Knutson* et. al [30], *Knorr* and *Harris* [31])
- this layer chromatography: $I_{fl} = I_{fl}(\lambda_{em},R_f)$ (*Gianelli* et. al [32])
- reaction mixtures: $I_{fl} = I_{fl}(\lambda_{em},t_{Rct})$ (*Ainsworth* [33])

2.5. Synchronous Excitation Spectra

As *Weiner* [34] has pointed out, analytical information obtained by the «synchronous scan» technique introduced by *Lloyd* [35] may also be derived from 2D-spectra: A synchronous excitation spectrum corresponds to a cut in the 2D-spectrum along a straight line with $\lambda_{em} = \lambda_{ex} + \Delta\lambda$. Many analytical applications of this technique have been published [36-38], including a comprehensive review [39]. Fig. 5 shows the re-

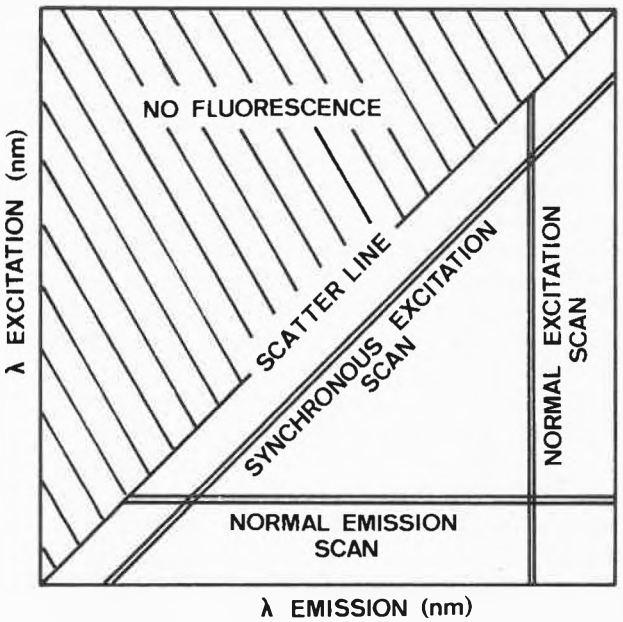

Fig. 5: Schematic representation of a two dimensional spectrum in relation to the conventional excitation and emission scans and to the synchronous excitation scan (see sec. 2.5).

lationship of conventional emission and excitation scan to synchronous scan detection.
Hornig and *Chrisholm* [40] have designed an instrument that allows the optical integration of a synchronous scan spectrum without moving any gratings.
In a recent paper, *Inman* and *Winefordner* [41] described a modified synchronous excitation experiment, in which the scan is performed with constant energy difference ($\tilde{\nu}_{em} = \tilde{\nu}_{ex} - \Delta\tilde{\nu}$). This technique has some advantages over the standard method, particularly, in the analysis of mixtures of polynuclear aromatic hydrocarbons. These compounds show well structured spectra with vibration bands of similar frequencies, which therefore lie on a straight line in the wavenumber- rather than in the wavelength-scale.

3.0 Applications

3.1. Analytical studies

TLS has been widely applied in the analysis of mixtures of polynuclear aromatic hydrocarbons in view of their importance as air pollutants. All of the instruments described in section 2.1 and the data analysis procedures in section 2.2 have been tested with such mixtures. The concentrations of up to six components have been accurately determined by *Ho* et. al [42] (fig. 3). Mixtures of N-Heterocycles have been studied by *Giering:* In order to observe the phosphorescence of non fluorescent compounds, the TLS were also recorded at 77K [3].
A second important application of TLS is the study of oil in water, which was promoted by *Hornig*: TLS has been utilized to monitor the concentration of crude oil in water [43] and to characterize oil samples coming from different sources [23].
The spectral analysis of mixtures of different porphines has been carried out [20, 32].
Biological material has also been studied by TLS: *Weber* [6] assigned the luminescence of serum albumin to a superposition of the emissions of tryptophan and thyrosine contained in the protein. *Davis* et. al [24] used TLS to characterize the aging process of nematodes.
Hersherberger et. al [18] applied TLS as a real rime monitor for the effluents in liquid chromatography.

3.2. The Edge Excitation Red Shift in the spectra N-heterocycles in Alcohol

This effect (EERS), namely the shift of the emission spectrum upon excitation into the red edge of the absorption spectrum, was first observed in the fluorescence spectrum of quinine in acid solution by *Chen* [44]. *Azumi* et. al [45, 46] suggested that different solvent-solute interactions in the ground and in the excited state (i.e. a dependence of the transition energy on the surrounding of the chromophore), in combination with incomplete solvent reorientation relaxation during the lifetime of the excited state, lead to the observed shifts.

In the case of N-heterocycles in protic solvents, it is well known [47, 48] that H-bond formation influences the transition energies. Therefore, the heterogenity in the sample due to this type of solute-solvent interaction may provide a large contribution to the EERS in these systems.

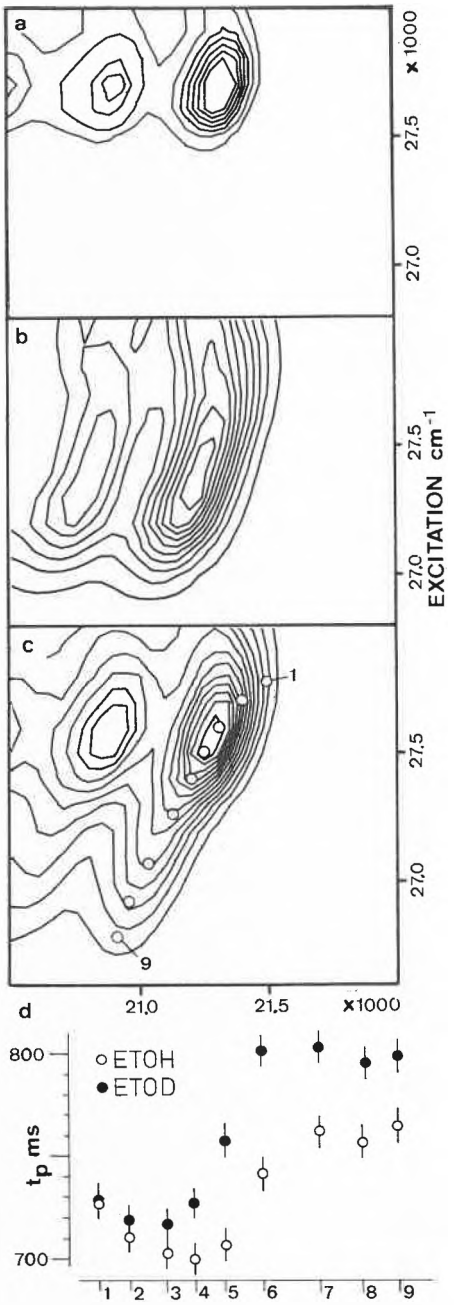

Fig. 6: Solvent dependence of the EERS in the phosphorescence of benzo(f)quinoxaline: (a) in 3MP, (b) in 2MTHF, (c) in ethanol (d) plot of the phosphorescence lifetime in EtOH and EtOD measured at the spectral points indicated in (c).

The 2D-spectra (fig. 6) show the solvent dependence of the EERS in the phosphorescence of benzo(f)quinoxaline. In order to determine if H-bond formation is responsible for the enhanced EERS in ethanol, the phosphorescence decay was observed in a series of points along the curve indicated in fig. 6c. The results

of these measurements in ethanol and monodeuterated ethanol (-OD) are plotted in fig. 6d: In contrast to the lifetimes observed in the high energy region the values obtained upon red edge excitation show a significant D-effect.
These results indicate that the EERS in the phosphorescence spectrum of benzo(f)quinoxaline is largely due to H-bond formation. Similar results were obtained from 1,4-diazatriphenylene in ethanol [49].

3.3. The dual phosphorescence of benzo[a]phenazine in ethanol

The use of TLS to study the influence of H-bond formation on the phosphorescence spectrum of benzo[a]phenazine was described in a recent paper [47]. Based on the translation symmetry in the 2D-spectrum (fig. 7), the total phosphorescence of this

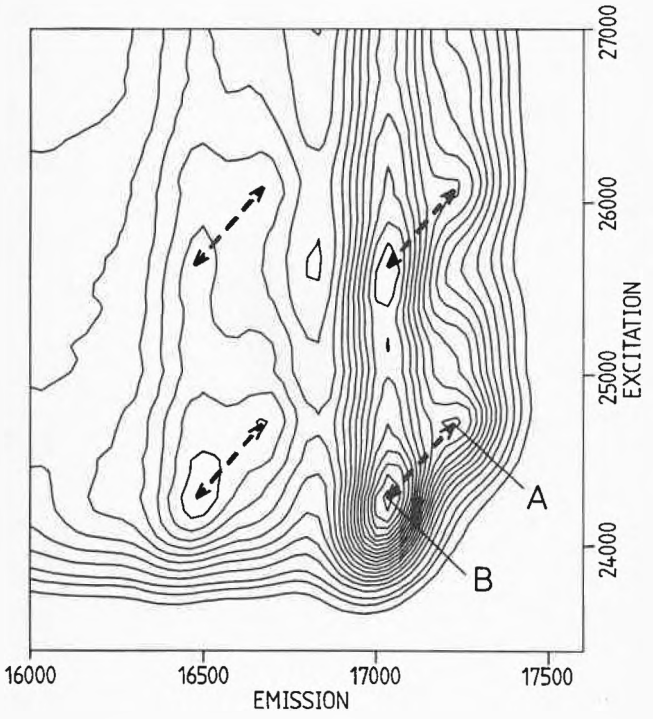

Fig. 7: 2D-spectrum of benzophenazine in ethanol at 77K. The maxima of the 0-0 bands are marked. A: free form, B: H-bonded form of benzophenazine. The dashed arrows indicate the translation symmetry between the two subspectra (from [47]).

molecule in ethanol has been shown to consist of two structurally identical subspectra, which are shifted relative to each other. From the solvent dependence of the spectrum, the red shifted subspectrum was assigned to H-bonded benzophenazine molecules. This assignment was supported by the deuterium effect on the lifetimes of the two emissions in EtOH and EtOD. TLS was also applied in similar studies on the phosphorescence of H-bonded species of 8-methoxybenzophenazine and phenazine in ethanol [49].

3.4. Analysis of Multisite Shpolskii-Spectra

Shpolskii-matrices [50] are widely used in low temperature luminescence spectroscopy, since they provide highly resolved spectra. However, usually more than one crystalline site is occupied by the guest molecules, and, therefore, the spectra obtained consist of a superposition of several similarly structured subspectra. Due to the large number of bands, such multisite spectra are difficult to analyse, and the resulting long peak listings are not easy to survey. Very often the exact assignment of certain lines is impossible without single site spectra. Such spectra may be obtained either by selective excitation, usually provided by a laser, or by a deconvolution of the multisite spectrum with the site pattern [51, 52]. Their interpretation in terms of molecular vibrations is straightforward. The information about the site pattern is however lost.
Fig. 8 shows the 2D-spectrum of the phosphorescence of benzo(a)phenazine in n-hexane at 4K. The spectrum covers the region of the $S_{10} \leftarrow S_{00}$ excitation and the $T_{10} \leftarrow S_{00}$ emission. The assignement of the individual lines to the different sites in table 1 is in agreement with a previous analysis [53]:

Table 1: Analysis of the site structure of the phosphorescence spectrum of BPH in n-hexane*

Site	Lines
1	1,15,17,21,26,27
2	2
3	4,20,25
5	13

* The numbers refer to the multisite spectrum in [53]

The correlation of the lines in the $S_1 \leftarrow S_0$ and in the $T_1 \leftarrow S_0$ multiplet is evident: The transition energies of sites 1, 3, and 5 decrease in the same order for both transitions, but the site splitting is much larger in the phosphorescence than in the $S_1 \leftarrow S_0$ absorption. Sites 2 and 4 range in this series; their $S_1 \leftarrow S_0$ transitions are red-shifted with respect to the corresponding transitions of the three main sites**.
The projections of the 2D-spectrum along the two axes show the features of the multisite spectrum [53] as expected.
In the 2D-spectrum of *Shpolskii*-spectra, both the detailed information about the virational structure of the subspectra and the site pattern that is characteristic for a particular host-guest system may be visualized in a concentrated form. Moreover, since the site-pattern in general depends on the electronic transition [54], the correlation of the individual lines in different patterns is readily displayed in TLS.
Finally, various types of data processing may be carried out to extract the desired information form the

** The $(S_1 \leftarrow S_0)_4$-transition is very weak and lies at 24200cm^{-1}, i.e. outside the range of the 2D-spectrum in fig. 8.

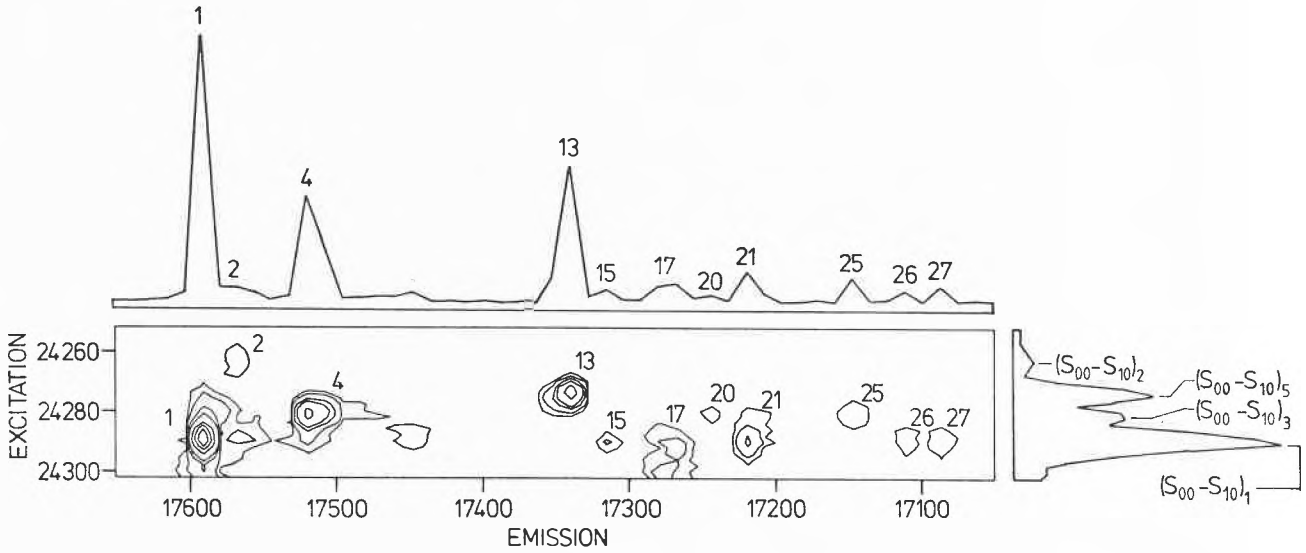

Fig. 8: 2D-phosphorescence spectrum of benzo(a)phenazine in n-hexane at 4K. The region of the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ transition is shown.

2D-spectrum. For example, applying procedures similar to those used in derivative spectroscopy, broadband background may be supressed or reduced.

3.5. Analysis of Energy-Selection Spectra

At low temperature, the bandwidth of emission spectra often is dominated by inhomogeneous broadening. However, using the technique of optical site-selection [55,56] or energy-selection spectroscopy [57], highly resolved spectra may be obtained which, within the range of the inhomogeneous bandwidth, shift parallel to the excitation frequency. As has been pointed out [58], the structure of such spectra may become very complicated upon excitation in an absorption region where several inhomogeneously broadened bands overlap. Under these conditions, the emission consists of a superposition of different subspectra, all having the same structure but shifted with respect to each other.

2D-spectra may be used to represent these features clearly and to assign the various bands in a complicated spectrum to the inherent subspectra. An example the energy-selection fluorescence spectrum of pyrene in ethanol at 6K is shown in fig. 9. The excitation frequency was 27380cm^{-1}. Thus, the spectrum corresponds to a section along the axis indicated in fig. 10. The analysis may now be carried out by starting from the peak positions of the one dimensional spectrum and searching the next relative maximum in the 2D-spectrum along lines with $\tilde{\nu}_{ex} - \tilde{\nu}_{em} = \text{const.}$

Hence, the spectrum in fig. 9 is a superposition of 4 subspectra which correspond to subsets optically selected by excitation into the following vibrational levels of the S_1-state:

a) $S_{00} \rightarrow S_{10} + 393\ \text{cm}^{-1}$
a) $S_{00} \rightarrow S_{10} + 449\ \text{cm}^{-1}$
a) $S_{00} \rightarrow S_{10} + 488\ \text{cm}^{-1}$
a) $S_{00} \rightarrow S_{10} + 572\ \text{cm}^{-1}$

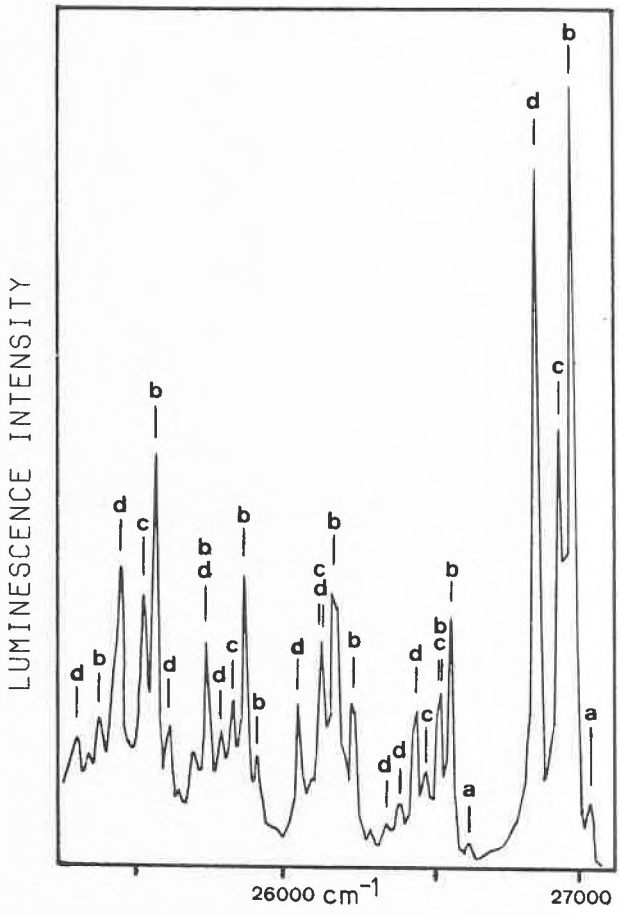

Fig. 9: Energy-selection fluorescence spectrum of pyrene in ethanol at 6K excited at 27380cm^{-1}. The bands are assigned to four subspectra a-d (see text).

This type of analysis may be useful in cases where no «single site» spectrum can be obtained by excitation

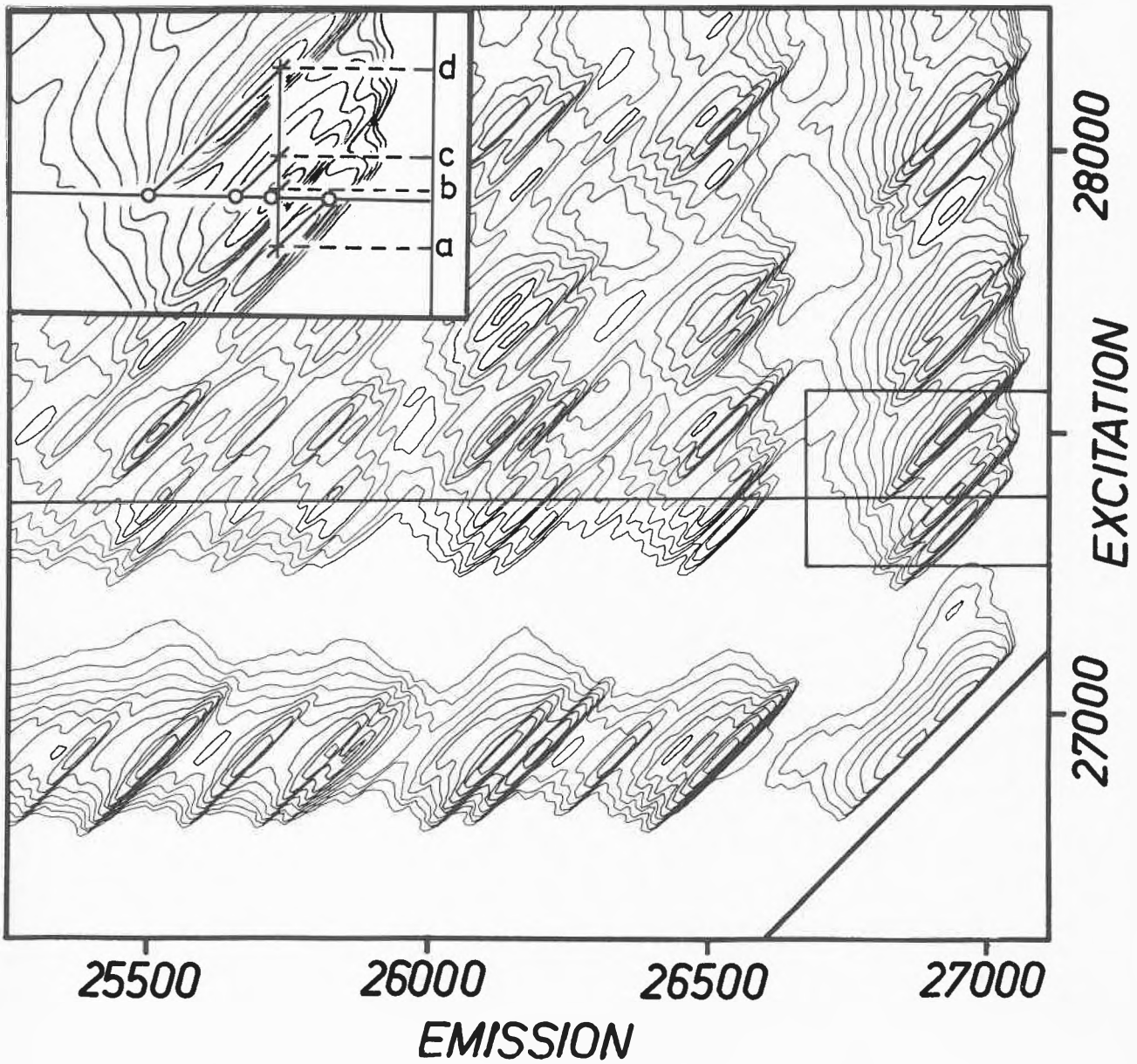

Fig. 10: Two-dimensional energy-selection spectrum of pyrene in ethanol at 6K. The scan for the 1D-spectrum in fig. 9 is indicated. Inserted: Graphical procedure for the assignement of the 0-0 bands in the 1D-spectrum to various subspectra.

in the region of the 0-0 transition either because this spectral region is not accessible by the excitation source or due to low lying vibrational levels and large overlap of the corresponding inhomogeneous bands. Moreover, solvent Raman bands can easily be distinguished from fluorescence lines in the 2D-spectrum.

4.0 Conclusions

Total Luminescence Spectroscopy (TLS) is shown to be an extremely useful technique in the analysis not only of multicomponent systems, but also in the investigation of photophysically interesting effects that lead to excitation dependent emission spectra. TLS allows the representation of complex luminescence properties of a sample in a concentrated and easily interpretable form. The application of multichannel detectors, such as vidicons and diode arrays, greatly decreases the data acquisition time for good 2D-spectra. With improvements in the solid state detector technology, the importance of TLS as an analytical and research technique will certainly increase.

5.0 Acknowledgement

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