ATTI ACCADEMIA NAZIONALE DEI LINCEI

CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

RENDICONTI

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The feasibility of obtaining emission spectra of organic crystals using a spectrofluorometer

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **57** (1974), n.5, p. 447–451.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1974_8_57_5_447_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1974.

Chimica. — *The feasibility of obtaining emission spectra of organic crystals using a spectrofluorometer.* Nota di SERGIO DELLONTE (*) e GABRIELE GIRO (*), presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Viene dimostrata la possibilità di registrare gli spettri di emissione di sostanze organiche allo stato cristallino mediante l'uso di uno spettrofluorimetro. Come esempio dei risultati ottenibili vengono mostrati gli spettri di emissione di monocristalli di antracene.

INTRODUCTION

The appearance on the market of an automatic apparatus capable of registering both emission and excitation spectra, also corrected, has brought new impetus to the study of luminescence of organic substances.

Usually this type of apparatus has been used only for the study of luminescence of solutions [1].

In this work we describe an adaptation of a spectrofluorometer for studying luminescence in organic aromatic solids and demonstrate the validity of this technique in getting emission spectra of anthracene single crystals.

EXPERIMENTAL

The apparatus used was a G. K. Turner spectrofluorometer « Spectro Model 210 Turner Assoc. ».

The schematic diagram in fig. 1 (*a*) shows the optical arrangement of the apparatus used for measuring luminescence [1].

The crystal attached by an optically transparent silicon grease on a quartz support was mounted on a special designed cell at an angle of 45° with respect to the incident light and the photomultiplier, as shown in fig. 1 (*b*).

The mirror (E) shown in fig. 1 (*a*) is used in the case of solutions to collect the light emitted by the substance in the opposite direction to the photomultiplier in order to increase the sensitivity of the instrument. In the case of solids however, the mirror serves no useful purpose, first because of the high intensity of emission compared with that obtained from solutions [2] and second because it causes spectra distorsion as it will be explained later.

In order to obtain corrected spectra, in which the variable lamp intensity and the spectral response of the photomultiplier are taken into account, the substance under study must have a transmission of not less than 95 % at the wavelength of excitation in order that the correction of the system (lamp, bolometer and photomultiplier) is valid [1].

For solids, which are in general " opaque " it has been possible to obtain corrected spectra using sufficiently small crystals.

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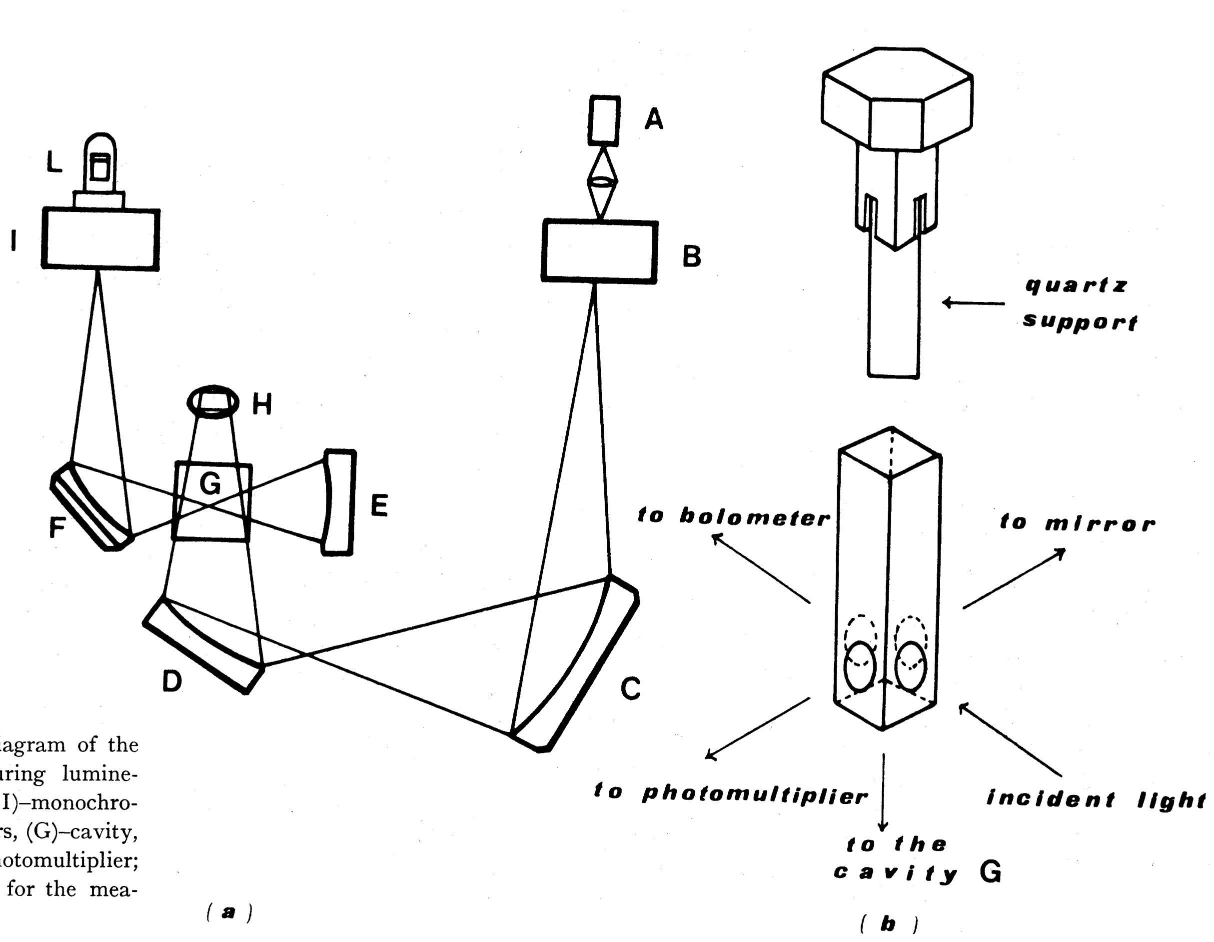

Fig. 1. – (*a*) Schematic diagram of the optical system for measuring luminescence. (A)–source, (B , I)–monochromators, (C, D, E, F)–mirrors, (G)–cavity, (H)–bolometer, (L)–photomultiplier; (*b*) View of the cell used for the measurement of crystals.

To demonstrate that the spectrofluorometer so modified can supply good spectra in the case of solids, measurements have been carried out using highly pure anthracene single crystals. The choice was made because the luminescent properties of this substance are already well known [2].

The thickness of the anthracene single crystals used was about 2 mm. All the spectra were obtained irradiating at 365 nm with a bandwidth of excitation of 100 Å registering the emission with a bandwith of 5 Å.

RESULTS AND DISCUSSION

The emission spectrum obtained with the arrangement shown in fig. 1 is displayed in fig. 2 (*a*). The spectrum shows a distortion between 400–440 nm and a poor resolution of the bands at 404 and 425 nm.

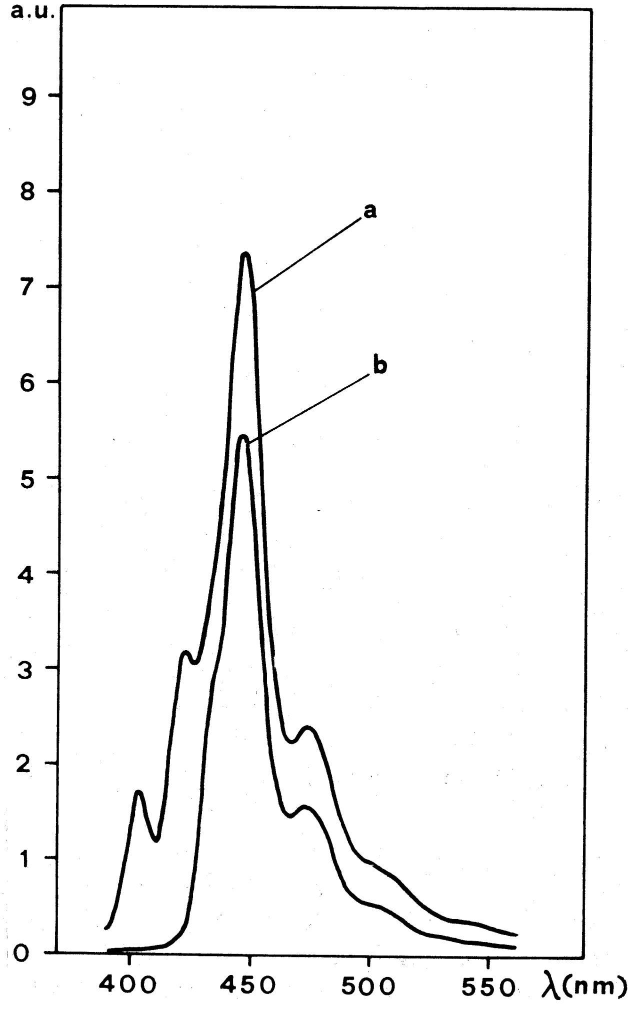

Fig. 2. – (*a*) Spectrum obtained with the arrangement of fig. 1; (*b*) Spectrum obtained from the crystal surface opposite to that irradiated.

The reason of it is due to the reabsorption of the light at these wavelengths and to the effect of the mirror. In fact reabsorption, a characteristic of anthracene single crystals and generally of high fluorescence quantum yield substances, leads to the complete disappearance of the first emission band while the second appears severely weakened [3].

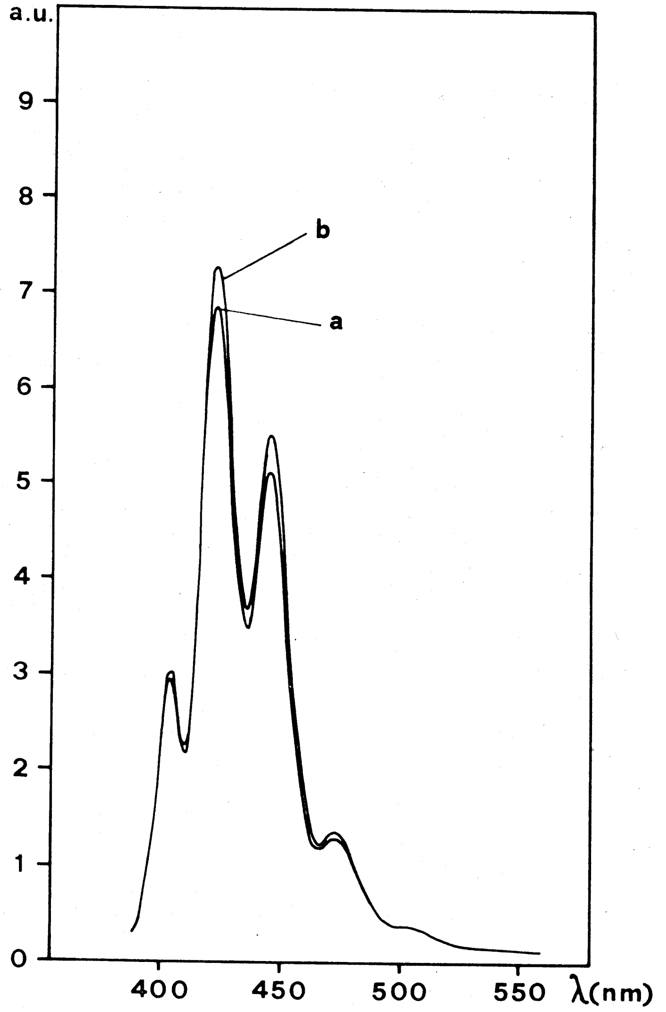

Fig. 3. – Spectra obtained without the mirror (E) of fig. 1 (*a*); (a) Corrected; (*b*) Uncorrected.

The mirror effect may be described as follows, the exciting light is absorbed in the first few microns of the surface, the emission in the direction away from the photomultiplier is filtered by the crystal itself [2] (inner filter effect) and only the light at wavelengths longer than about 440 nm reaches the mirror, is reflected and added to the light of equal wavelength emitted from the excited surface. Therefore the recorded spectra show relative enhancement at the longer wavelengths with respect to the shorter ones.

This leads to the distortion of the spectrum in which the latter bands may appear as shoulders of the former.

The light reflected by the mirror is shown in fig. 2 (*b*), this spectrum has been obtained from the crystal surface opposite to that irradiated. It is possible to see the complete reabsorption of the light at wavelengths below 440 nm.

The true spectrum is the difference between the spectra (*a*) and (*b*) of fig. 2 and it is equal to that obtained under the same conditions, excluding the mirror, and this is shown in fig. 3 (*a*).

Fig. 3 (*a*) shown the corrected spectrum while fig. 3 (*b*) shows the uncorrected one of the same crystal, obtained excluding the bolometer [1]. As we can note, the difference between the two spectra is almost negligible, this is due to the fact that the photomultiplier spectral response may be considered constant because of the correction inherent in the apparatus [1].

Both spectra of fig. 3 are in excellent agreement with those previously obtained by different techniques [3, 4].

We have therefore reached the conclusion that the use of the spectrofluorometer for work with organic solids is of great value because of its speed of performance, sensitivity and precision with which it is possible to register emission spectra.

Furthermore, as it is possible to determine approximately the energy of the O—O transition of the first singlet state, we see a useful application in the qualitative detection of unknown substances and in the control of the purity of organic single crystals during the various stages of their preparation [5, 6].

Acknowledgements. The Authors would like to thank Prof. G. Semerano for his helpful discussion, Dr. Z. S. Weisz of the Puerto Rico Nuclear Center for having provided the anthracene crystals, Messr.s G. Gualandi and L. Ventura for production of mechanical parts used in this study.

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