ELSEVIER

Spectrochimica Acta Part A 54 (1998) 1443–1449

SPECTROCHIMICA
ACTA
PART A

The Sphol'skii fluorescence spectrum of cyclopenta[c,d]pyrene. Novel evidence for anomalous S_2-emission

Cees Gooijer [a],*, Igor Kozin [1],[a], Nel H. Velthorst [a], Martin Sarobe [b], Leonardus W. Jenneskens [2],[b], Edward J. Vlietstra [b]

[a] *Department of General and Analytical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*
[b] *Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 16 October 1997; accepted 17 February 1998

Abstract

The high resolution Sphol'skii fluorescence spectrum of the non-alternant polycyclic aromatic hydrocarbon cyclopenta[c,d]pyrene (CPP, **1**) in an *n*-hexane matrix at cryogenic temperature is reported. Two distinct narrow spectral lines at 378.0 and 379.6 nm representing two sites were found, whereas in *n*-octane no Sphol'skii effect was observed. In accordance with reported data on the fluorescence of CPP (**1**) these lines have to be assigned to anomalous S_2-emission. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Sphol'skii fluorescence; Cyclopenta[c,d]pyrene; S_2-emission

1. Introduction

Among the plethora of (non)-alternant polycyclic aromatic hydrocarbons (PAH) several representatives exhibit anomalous fluorescence, i.e. emission from the higher excited singlet S_2-state, instead of (or in addition to) emission from the S_1-state. A seminal example is the non-alternant PAH azulene. Upon excitation it gives strong S_2-emission, which is rationalized on the basis of the large energy difference between the S_1- and S_2-states ($E_{S_2}-E_{S_1}=\Delta E_{\mathrm{gap}} \sim 10000\ \mathrm{cm}^{-1}$) [1]. However for other representatives, the situation is less clear. It is not always evident whether anomalous fluorescence or fluorescence of a trace-level amount impurity with a high fluorescence quantum yield (Φ_F) is responsible for the emission. For instance, the long-standing controversy concerning the emissive properties of fluoranthene for which earlier two emissions have been reported at 350 and 410 nm was put to an end by some of us [2]. Sphol'skii spectroscopy—a cryogenic high-resolution molecular luminescence technique [3]—unambiguously showed that the 350 nm emission is not due to anomalous S_2-emission, but a consequence of a strongly fluorescent impurity—most probably acephenanthrene. This ex-

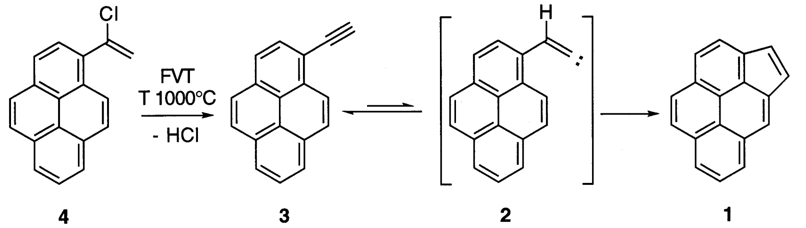
---

* Corresponding author. Tel.: +31 20 4447540; fax: +31 20 4447543; e-mail: gooijer@chem.vu.nl/aac@chem.vu.nl

[1] Present address: Department of Chemistry, Queen's University, Kingston, K7LN6 Ontario, Canada.

[2] Tel.: +31 30 2533128; fax: +31 30 2534533; e-mail: jennesk@chem.run.ul

1386-1425/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S1386-1425(98)00045-6



Scheme 1.

ample underlines the potential of Sphol'skii fluorescence spectroscopy for the identification of PAH and interfering fluorescent impurities.

In addition, high-resolution PAH Sphol'skii fluorescence data are of interest from an analytical point of view. It is well documented that PAH are invariably generated during incomplete combustion of hydrocarbon containing fuels and that specific representatives are primarily responsible for the genotoxicity of these combustion samples [4]. Hence, in situ PAH identification in complex samples using Sphol'skii fluorescence spectroscopy has become an important research subject [5]. A drawback, however, is the availability of pure PAH for the determination of reference data.

Among the ubiquitous PAH generated during combustion the non-alternant cyclopenta[*c*,*d*]pyrene (CPP, **1**) has been recognized to contribute substantially to the genotoxicity of the samples [6]. With regard to the origin of CPP (**1**) under high temperature conditions in the gas phase the intermediacy of 1-ethynylpyrene (**3**) obtained via either C_2 or ethyne (C_2H_2) addition to pyrene has been invoked [7]. This proposal was supported by flash vacuum thermolysis (FVT) of 1-chloroethenylpyrene (**4**) being a 'masked' 1-ethynylpyrene. Under unimolecular FVT conditions (1000°C, 10^{-2} Torr) 1-choroethenylpyrene (**4**) is efficiently converted into CPP (**1**, mass recovery 88%) via a consecutive process, i.e. facile hydrogen chloride elimination ($\mathbf{4} \rightarrow \mathbf{3}$) followed by ethynyl ethylidene carbene equilibration ($\mathbf{3} \rightarrow \mathbf{2}$) and ultimately carbene C–H insertion ($\mathbf{2} \rightarrow \mathbf{1}$, Scheme 1) [8]. The accessibility of CPP (**1**) on a gram scale prompted us to reinvestigate its anomalous emissive properties using Sphol'skii fluorescence spectroscopy. In the case of CPP (**1**), instead of S_1-state fluorescence which is absent, evidence for a very weak though measurable anomalous S_2-state fluorescence near 25000 cm^{-1} (400 nm; quantum yield Φ_F 0.003 and lifetime τ of ~ 3 ns) has been reported [9]. Unfortunately, cryogenic absorption spectra of CPP (**1**) provide little additional information compared with spectra recorded at room temperature. Upon cooling a 10^{-4} M solution of CPP (**1**) in *n*-octane to 77 K, there is hardly any improvement of spectral resolution [10]. At 5 K, weak Sphol'skii-type features in the 460–550 nm spectral range can be observed. It should be noted, however, that the latter spectra were obtained for saturated solutions of CPP (**1**) in *n*-octane [10]. Under these conditions, complicating factors like aggregation of CPP (**1**), which is detrimental for the Sphol'skii effect, and the possible presence of impurities in the sample showing the Sphol'skii effect cannot be excluded.

Here we report the Sphol'skii fluorescence spectrum of CPP (**1**). It is shown that the anomalous emission occurs from the S_2-state.

2. Experimental

2.1. Chemicals

By recording fluorescence emission-excitation spectra the purity of the solvents (*n*-octane, *n*-hexane and dichloromethane) was checked. No significant response was observed and the solvents were used without further purification.

2.2. Flash vacuum thermolysis of 1-chloroethenylpyrene (4)

FVT (unpacked quartz tube (length 40 cm, diameter 2.5 cm), 1273 K and 10^{-2} Torr, sublimation temperature 130°C) of 1-chloroethynylpyrene (**4**, 1.5 g, 5.8 mmol) gave CPP (**1**, 1.16 g, 5.1 mmol, mass recovery 88%). Satisfactory analytical data (^1H and ^{13}C NMR, GC-MS, IR), which were in line with those previously reported [8], were obtained. For the fluorescence measurements crude CPP (**1**) was further purified by preparative column chromatography (silica, eluens *n*-hexane:chloroform 1:1 v/v). The UV/Vis absorption spectrum of CPP (**1**, solvent *n*-hexane, 10^{-4} M, room temperature) was recorded on a Cary 1 spectrophotometer (Table 1).

2.3. Liquid chromatography separation

For normal-phase liquid chromatography (LC), a Sigma-Aldrich Nucleosil NH2 column (5 mm particle size, 250 × 4.6 mm i.d.) equipped with a 100 μl injection loop was used. The hardware consisted of two Applied Biosystems Model 400 Solvent Delivery Systems, and a multi-wavelength Applied Biosystems Model ABI1000S Diode Array Detector (5 nm bandpass).

Table 1
PPP/SCF CI vertical excitation energies and oscillator strengths of CPP (**1**)[a]

PPP λ [nm]	Oscillator strength f	Experimental λ [nm] {log ε}
452.9 (505)[b]	0.086	450 {2.77}
369.9 (386)[b]	0.360	386 {3.37}
354.8 (352)[b]	0.365	373 {4.06}
		363 {3.99}
		351 {4.20}
		341 {4.06}
269.7 (308)[b]	0.189	291 {4.22}
266.2 (295)[b]	0.439	279 {4.16}
253.8 (276)[b]	0.338	237 {4.66}
226.2 (247)[b]	0.138	221 {4.81}
219.2 (217)[b]	0.717	
213.5	0.314	
212.0	0.636	
208.9	0.432	
200.6	0.324	

[a] For the PPP/SCF CI calculation of CPP (**1**) a standard was used (pyrene part: C–C 1.40 Å, C–C–C-valence angles 120°, fused cyclopentene moiety: C–C 1.45 Å, C = C 1.35 Å and C–C–C-valence angles 108°). For the calculation of the optical properties full single CI was carried out [11]. [b] Vertical excitation energies of CPP (**1**) from Ref [9] (no numerical values of the oscillator strengths *f* are reported).

Isocratic elution was carried out with a mixture of *n*-hexane and dichloromethane (9:1 v/v) at a flow rate of 1.5 ml min^{-1}. The effluent was usually monitored at 254 nm. Chromatographic fractions containing PAH were collected into separate vials and submitted either to reversed-phase LC or Sphol'skii fluorescence measurements.

Reversed-phase LC was carried out using a Varian Star LC system (Star 9012 Solvent Delivery System), a Varian Mistral Column Thermostat, a Star 9100 Autosampler, a Separations GT-103 Degasser, a Vydac 250 × 4.6 mm i.d. RP C18 column and a Varian 9065 Polychrom Diode Array Detector (4 nm bandpass). The level of acetonitrile was increased stepwise gradually from 65% in the beginning of separation up to 100% at the end of the run. The effluent was monitored at λ 254 nm.

2.4. Sphol'skii fluorescence detection

For cryogenic fluorescence measurements, the fractions collected after carrying out normal-phase LC were dried in a gentle flow of N_2, and redissolved in either *n*-hexane or *n*-octane. A 450 W Xenon arc lamp coupled with a Bausch & Lomb monochromator (5 nm bandpass) provided lamp excitation.

A closed-cycle helium CTI cryogenics refrigerator was employed to simultaneously cool down to 15–25 K 4 × 10 μl sample solutions and the cold tip of a cryogenerator was provided by using a gilded copper sample holder covered with sapphire windows [3]. For luminescence detection, the emission signal from a front-face illuminated sample was focused on the entrance slit of a Jobin-Yvon HR1000 monochromator (0.08 nm resolution) and measured by an EG&G (Princeton, NJ) Model 1421B blue-enhanced intensified linear photodiode array. This enables simultaneous data acquisition from about 20 nm wide spectral regions. The spectral data were collected and processed by employing a Model 1463 detector controller and a Model 1460 OMA III control system.

3. Results and discussion

Evidence for anomalous S_2-emission from CPP (**1**) after excitation was previously obtained from steady-state and time-resolved fluorescence spectroscopy on liquid-state samples at room temperature. The steady-state excitation spectrum showed reasonable agreement with the absorption spectrum in the S_2 region [9]. The possible occurrence of S_2-emission is further supported by PPP/SCF CI calculations [11]. Vertical excitation energies and oscillator strengths f are found, which are in line with available experimental data (Table 1). Furthermore, the PPP/SCF CI results show significant configuration interaction for all calculated excitations. Note, however, that our PPP/SCF CI version, which was parameterized for the calculation of vertical excitation energies and oscillator strengths f of dye molecules, gave results in better agreement with experiment than those previously obtained with another PPP/SCF CI version [9]. The considerable $\Delta E_{\mathrm{gap}}(=E_{S_2}-E_{S_1})$ of ~ 5000–6000 cm^{-1} is in line with that required for anomalous S_2-emission [12].

A prerequisite for the unambiguous assignment of CPP (**1**) S_2-emission is to ascertain, that trace-level amounts of strongly fluorescent impurities are absent. The latter, if present, may produce fluorescence signals of comparable intensities with that assigned to CPP (**1**) S_2-emission. This is of special importance for CPP (**1**), since it is prepared from a substituted pyrene (**4**, Scheme 1). Note that pyrene possesses a fluorescence quantum yield Φ_F 0.10 for S_1-emission [13]. Fortunately, Sphol'skii fluorescence spectroscopy possesses additional selectivity [3]. Whereas the spectra are highly resolved due to the Sphol'skii effect, this effect will only be observed for fluorophores that fit well in the n-alkane matrix. For example a survey of available atlas of reference spectra [10,14], reveals that polar fluorophoric molecules do not meet this requirement. In fact, in view of the demands involved in the present study, most probably only parent PAH and their alkylated (possibly including their ethenylated and ethynylated derivatives) have to be accounted for.

To determine if strongly fluorescent PAH-like impurities in trace-level amounts are still present in our CPP (**1**) sample both normal-phase and reversed-phase column liquid chromatography (LC, UV absorption detection λ 254 nm) at high sensitivity was used. The expanded normal-phase chromatogram of CPP (**1**) obtained after preparative colum chromatography, is depicted in Fig. 1(A). Clearly, besides the main peak at 6.5 min, which corresponds to CPP (**1**), trace-level amounts of impurities, which also absorb at λ 254 nm, are present. Therefore, three fractions (1, 2 and 3) (Fig. 1(A)), which represent the effluent parts from 4.5 to 6.25 min, 6.45 to 6.70 min and 7.25 to 15.0 min, respectively, were isolated and subsequently subjected to Sphol'skii fluorescence analysis. For the normal-phase effluent fraction 2 only a single chromatographic peak assigned to CPP (**1**) was also found under reversed-phase LC conditions; this strongly corroborates the absence of additional impurities (Fig. 1(B)).

The Sphol'skii fluorescence spectra obtained in n-octane for fractions 1, 2 and 3, respectively, are shown in Fig. 2. From the data it can be concluded that fraction 1 contains pyrene and substituted pyrene derivatives (λ_{exc} 339, 344 and 349 nm, Fig. 2(A)) [15]. Note that under Sphol'skii conditions pyrene is efficiently excited at 339 nm (providing a 0–0 fluorescence transition at 372 nm in n-octane), whereas it can be hardly excited at 349 nm—a wavelength adequate for the excitation of ethylpyrene (0–0 transition in n-octane at ~378 nm and a vibronic transition at ~383 nm) [15]. Hence, the Sphol'skii fluorescence spectrum does not allow discrimination between various ethylpyrene isomers. Furthermore, the presence of substituted pyrene containing either an ethynyl or a 1-chloroethenyl moiety cannot be excluded (Scheme 1).

In fraction 3, among others, benz[a]pyrene was unambiguously identified—note the 0–0 emission band at 403 nm and a vibronic band at 408 nm (λ_{exc} 348 and 298 nm, respectively, Fig. 2(B)) [15]. We refrain from a structural elucidation of the constituents in fractions 1 and 3, since it is beyond the scope of this paper. Of interest are the Sphol'skii fluorescence spectra obtained for fraction 2

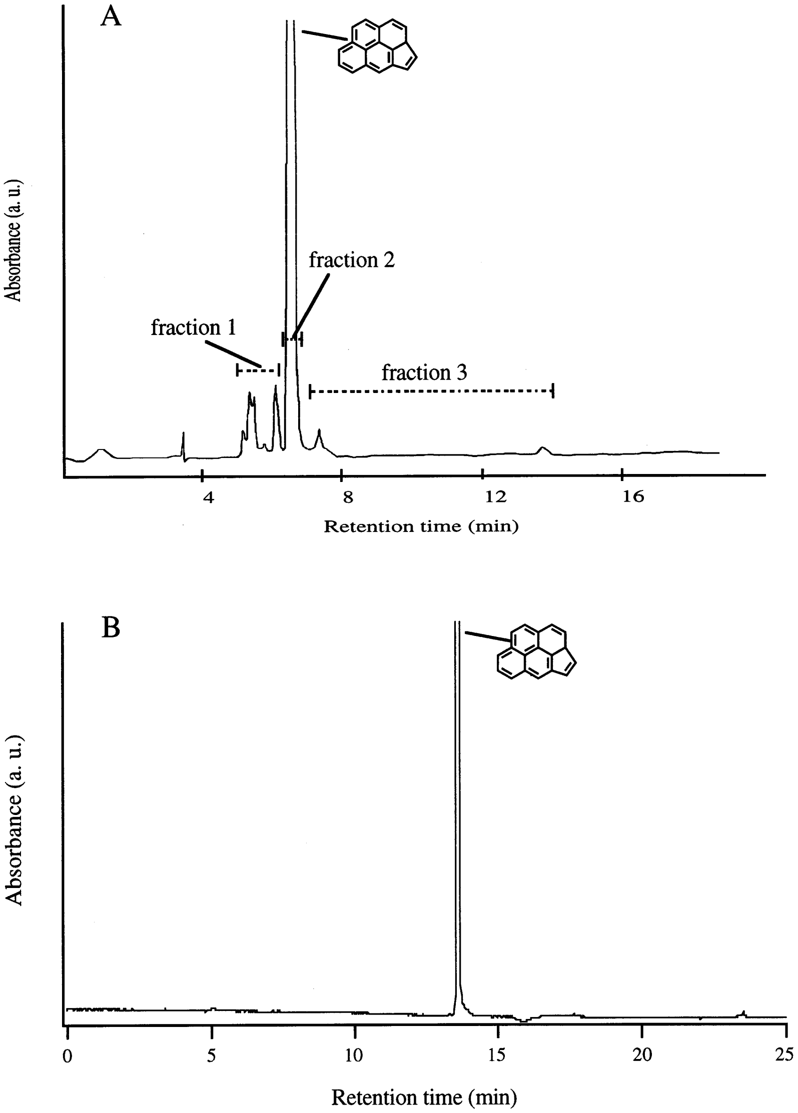


Fig. 1. Normal-phase chromatogram of CPP (**1**) and related impurities (A) and reversed-phase chromatogram of fraction 2 containing CPP (**1**; B, see Section 2).

(Fig. 2(C)). In the *n*-octane Sphol'skii matrix (λ_{exc} 333 nm) no sharp features are discernible and the possible evidence for the presence of fluorescent solutes is only suggested by the irregular baseline. The absence of distinct narrow lines, such as those observed for fractions 1 and 3, unequivocally shows that in fraction 2 no related strongly fluorescent impurities—alkylated PAH—are present. In agreement with the HPLC data the normal-phase chromatographic separation procedure to purify CPP (**1**) has been adequate. Remarkably, however, upon changing the Sphol'skii matrix from *n*-octane to *n*-hexane distinct narrow spectral lines positioned at 378.0 (26459 cm^{-1}) and 379.6 nm (26346 cm^{-1}) were recorded for fraction 2 (λ_{exc} 333 nm; Fig. 2(C)). Note that the blank *n*-hexane Sphol'skii fluorescence spectrum did not show any narrow-banded emissions. Such

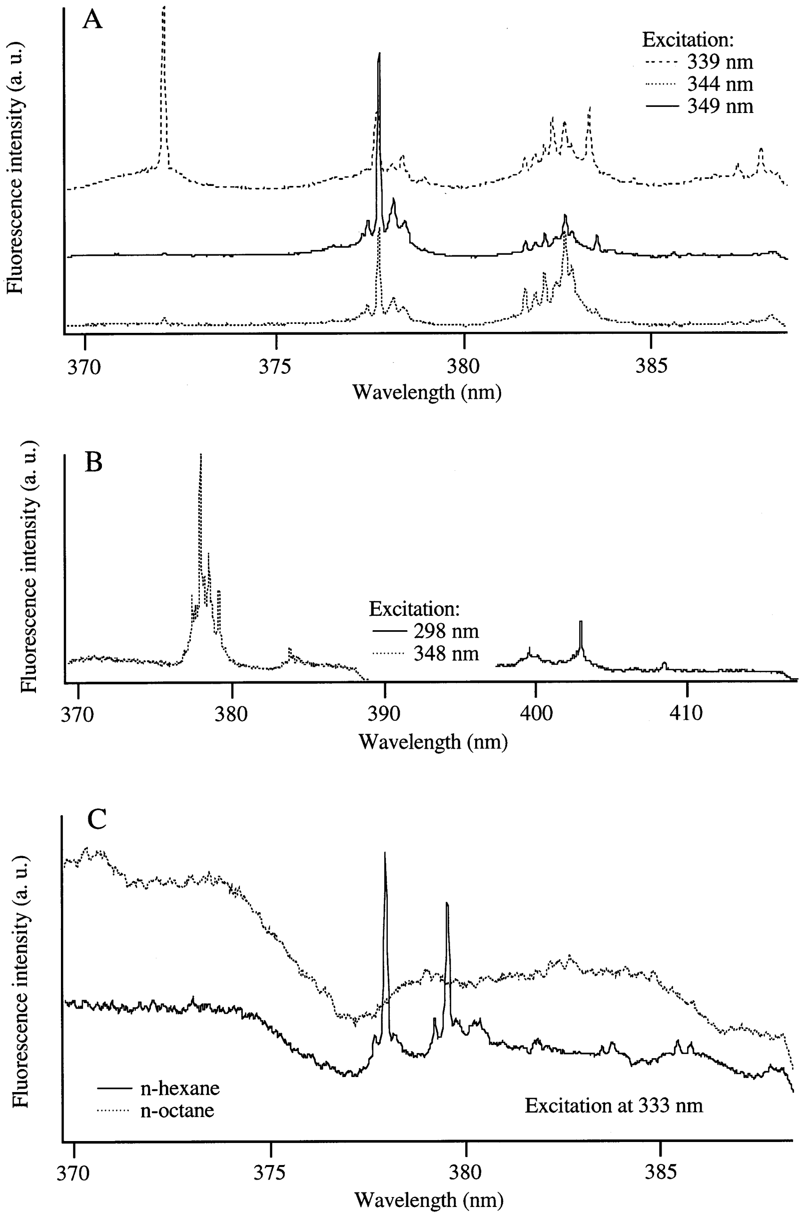


Fig. 2. Sphol'skii fluorescence spectra of PAH impurities contained in the normal-phase LC fractions 1 (A) and 3 (B; matrix *n*-octane), and fraction 2 (C; matrix either *n*-octane or *n*-hexane).

an extreme solvent influence is exceptional; for 'regular' PAH (type A molecules), exchange from *n*-octane to *n*-hexane typically induces only changes in (multiple) site structures in the emission spectrum, while narrow spectral features remain discernible. Only for compounds denoted as type B molecules in Ref. [16], the appearance of the Sphol'skii spectrum depends critically on various experimental parameters, such as the choice of matrix and the rate of matrix solidification upon cooling. This is attributed to the fact that type B molecules possess molecular dimensions that are incompatible with the crystalline (*n*-alkane) host matrix. In a simplified explanation part of them occupy positional sites in the solid matrix exhibiting *quasi*-lines, while the other part are isolated molecules present in intercrystalline amorphous positions, thus giving rise to broad bands. The ratio of both fractions is strongly influenced by the matrix choice. A well known example of a type B molecule is acenaphthene, whose Sphol'skii spectra have been thoroughly studied [17]. Thus under the assumption that CPP (**1**) behaves as a type B molecule, the results presented in Fig. 2(C) can be rationalized. At any rate, fraction 2 does not contain any 'regular' type A molecule.

Hence, the lines observed at 378.0 and 379.6 nm in Fig. 2(C) have to be ascribed to CPP (**1**) emission. In view of the available absorption and fluorescence data or CPP (**1**, Refs. [9,10] and Table 1), they unequivocally reflect anomalous emission coming from the S_2-state. The two lines represent 0–0 transitions from two sites. This is in accordance with the type B character of CPP (**1**). In comparison with the fluorescence spectra recorded for fractions 1 and 3 the line intensities are weak, despite the fact that CPP (**1**) strongly dominates (Fig. 1(A)). These results are not totally unexpected in view of the small quantum yield (Φ_F 0.003) for S_2-fluorescence reported [9]. Finally, the observation that the 378.0 and 379.6 nm lines are rather sharp is in agreement with literature data. Because of the relatively long emission lifetime $\tau \sim 3$ ns [9], spectral lifetime broadening effects, which are usually important for emission from higher excited states, are negligible for CPP (**1**).

In summary, our results substantiate the previously reported data concerning the occurrence of anomalous S_2-state emission in the case of CPP (**1**) [9].

Acknowledgements

Gerard J. Stroomberg (Institute of Environmental Studies, Vrije Universiteit, Amsterdam, The Netherlands) for carrying out reversed-phase chromatography and financial support from the Basque Government (Beca para Formacion de Investigadores (M.S.)) are gratefully acknowledged.

References

[1] J. Griesser, U. Wild, Chem. Phys. Lett. 52 (1980) 117.
[2] J.W. Hofstraat, G.P. Hoornweg, C. Gooijer, N.H. Velthorst, Spectrochim. Acta 41A (1985) 801.
[3] C. Gooijer, F. Ariese, J.W. Hofstraat, N.H. Velthorst, Trends Anal. Chem. 13 (1994) 53.
[4] J.J. Jacob, Pure Appl. Chem. 68 (1996) 301.
[5] J.C. Fetzer, W.R. Biggs, Polycycl. Arom. Compd. 4 (1994) 3.
[6] J.B. Howard, J.P. Longwell, J.A. Marr, C.J. Pope, W.F. Busby Jr., A.L. Lafleur, K. Taghizadeh, Combust. Flame 101 (1995) 262.
[7] H. Bockhorn, F. Fetting, H.W. Wenz, Ber. Bunsenges. Phys. Chem. 87 (1993) 1067.
[8] M. Sarobe, J.W. Zwikker, J.D. Snoeijer, U.E. Wiersum, L.W. Jenneskens, J. Chem. Soc. Chem. Commun. (1994) 89.
[9] B.F. Plummer, Z.Y. Al-Saigh, J. Phys. Chem. 87 (1983) 1579.
[10] L.A. Nakhimovskii, M. Lamotte, J. Joussot-Dubien, Handbook of Low Temperature Electronic Spectra of Polycyclic Aromatic Hydrocarbons, Elsevier, Amsterdam, The Netherlands, 1989.
[11] J.E.M.J. Raaymakers, L.W., Jenneskens, PPP-MO Calculations for IBM-PC and Compatibles using OS/2, Quant. Chem. Program Exch. Bull. (1995) 15, 68; QCPE 156.
[12] G. Eber, S. Schneider, R. Dorr, Chem. Phys. Lett. 52 (1977) 59.
[13] J.B. Birks, Chem. Phys. Lett. 25 (1974) 315.
[14] W. Karcher (Ed.), Spectral Atlas of Polycyclic Aromatic Compounds, vol. 1, Reidel, Dordrecht, 1985; vol. 2, Reidel, Dordrecht, 1988; vol. 3, Reidel, Dordrecht, 1991.
[15] I.S. Kozin, C. Gooijer, N.H. Velthorst, J. Harmsen, R. Wiegers, Intern. J. Environ. Anal. Chem. 61 (1995) 285.
[16] J. Rima, L. Nakimovsky, M. Lamotte, J. Joussot-Dubien, J. Phys. Chem. 83 (1984) 4302.
[17] J.W. Hofstraat, I.L. Freriks, M.E.J. de Vreeze, C. Gooijer, N.H. Velthorst, J. Phys. Chem. 93 (1989) 184.