Eur. Phys. J. D **8**, 205–210 (2000)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Fluorescence of jet-cooled naphthalene: Emission spectra, lifetimes and quantum yields

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Received 15 April 1999 and Received in final form 16 July 1999

Abstract. Fluorescence spectra of naphthalene, $C_{10}H_8$, were obtained in the laboratory under conditions which provide an appropriate simulation of the cometary conditions: super-cooled gas phase molecules in a collision-free environment. Five spectra were recorded, the excitation energies ranging from 1422 to 5293 cm^{-1} above the first electronic state S_1 at 32 020 cm^{-1}. A comparison with previous jet-cooled naphthalene fluorescence spectra obtained by Beck *et al.* [1] and Hermine [2] shows that the former results are not consistent with the present ones. Spectra obtained by Beck *et al.* show weaker intensities at greater wavelengths compared to those obtained by Hermine and ourselves. We also measured the fluorescence lifetimes by recording the fluorescence decay as a function of time after the excitation of the molecules by monochromatic lasers and deduced the fluorescence quantum yields. A synthetic emission spectrum under solar irradiation is obtained for astrophysical implications.

PACS. 33.50.-j Fluorescence and phosphorescence; radiationless transitions, quenching (intersystem crossing, internal conversion) – 96.50.Gn Comets

1 Introduction

The presence of polycyclic aromatic molecules (PAHs) in the interstellar medium is nowadays well accepted [3–5]. Moreover, comets are considered to be constituted of interstellar material contained in the primitive nebula and have kept their initial composition since their formation at the same time as the solar system. The study of the physical and chemical composition of comets can provide insight on the formation of the solar system.

Infrared spectra of several comets show an emission feature at 3.28 μm corresponding to the signature of aromatic compounds [6–8].

In using ultraviolet spectra of Comet P/Halley taken by the three-channel spectrometer TKS on the spacecraft Vega 2, Moreels *et al.* [9] identified phenanthrene, $C_{14}H_{10}$, a three-cycle condensed PAH, as a possible carrier of a broad band emissive feature in the near ultraviolet that arises at short distances from the nucleus. They also suggested that naphthalene, $C_{10}H_8$, a two-cycle PAH, might be responsible for the 323 nm feature detected at distances from the nucleus less than 3000 kilometres.

Their proposal was based on laboratory spectra obtained by Beck *et al.* [1]. Since the excitation conditions for the laser-induced fluorescence spectra did not reproduce solar-like conditions, we decided to set up a laboratory experiment to obtain fluorescence spectra of naphthalene under excitation conditions more adequately reproducing the radiation field present in the coma. The experiment uses the supersonic jet technique which produces super-cooled gas phase molecules in a collision-free environment and provides valuable simulation of the cometary medium.

It should be noted that the photophysical behaviour of the naphthalene molecule, both in normal gas phase and under jet-cooled conditions, as a function of the excitation photon energy, has been the subject of many studies. A good compilation and summary of the status of non radiative transitions in this large molecule can be found in the review paper by Avouris, Gelbart and El-Sayed [10]. It is out of the scope of this report to re-analyze the details of this photophysics. But much care was taken to obtain reliable fluorescence intensity measurements, corrected from instrumental effects, in order to make a valid prediction of the fluorescence spectrum induced by solar light pumping of a freshly outgassed naphthalene molecules in a comet.

2 Experiment

The supersonic jet technique allows us to prepare gas samples at a very low temperature (a few K) and in the absence of collisions. A heated solid sample reservoir provides a vapor pressure of naphthalene which is diluted in a carrier gas ($P_0 = 5$ bars of helium) before passing through a pulsed nozzle of small diameter and into a vacuum chamber. The adiabatic expansion of the gas mixture

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from the nozzle produces a fast and very efficient cooling of the molecules. All the naphthalene molecules are then in the fundamental vibrational state of the ground electronic state S_0.

Laser excitation of the naphthalene molecules is achieved by focusing a tunable pulsed, frequency-doubled, dye laser beam onto the jet. The pulsed valve operation is synchronized with the laser pulses ($\simeq$ 10 ns at 15 Hz). When the wavelength of the laser corresponds to an allowed optical transition in the molecule, the molecule is excited and relaxes by emitting photons (fluorescence emission) and by non radiative transitions. The fluorescence excitation spectra are obtained in recording the fluorescence intensity *versus* the laser wavelength while it is scanned. The fluorescence spectra are obtained in recording the dispersed emission resulting from excitation at a fixed laser wavelength. The emitted fluorescence is collected onto the entrance slit of a grating monochromator. The spectral resolution is selected by adjusting the width of the entrance slit and the binning of the pixels of the UV-enhanced, liquid nitrogen-cooled, CCD array detector. The typical value used in these experiments is 0.1 mm corresponding to a spectral resolution of 0.4 nm. The spectral variation of the grating efficiency and of the detector sensitivity have been taken into account when reducing the emission spectra.

Fluorescence lifetimes are also measured by recording as a function of time, thanks to a digital oscilloscope, the decay of the intensity after the laser excitation. We compare the fluorescence decay curve of the transitory signal measured by a photomultiplier with a synthetic curve representing the bi-exponential decay of the fluorescence, convoluted by an instrument response function. This measure gives information on the competition between fluorescence and other radiationless phenomena, and also allows evaluation of the fluorescence quantum yields $Q_{\rm fl}$ of the molecule.

3 Results

3.1 Fluorescence emission spectra

We obtained fluorescence emission spectra of naphthalene when exciting different absorption bands of the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ electronic transitions (Tab. 1). Lower spectra in Figures 1a and 1b show the emission spectra of naphthalene when excited to its first electronically excited state S_1. The excitation wavelengths are $\lambda_{\rm exc} = 299.0$, and 292.9 nm, corresponding to excess energies above the origin of the $S_1 \leftarrow S_0$ electronic transition of 1422 cm^{-1} and 2122 cm^{-1} respectively. The narrow widths (0.5 nm, *i.e.* close to the instrumental resolution) of the bands present in these spectra show that the naphthalene molecules do not undergo efficient intramolecular redistribution.

Figure 1c (lower spectrum) shows the emission spectrum obtained with $\lambda_{\rm exc} = 278.4$ nm (3900 cm^{-1} excess energy), in the broad absorption profile characterizing the origin of the $S_2 \leftarrow S_0$ electronic transition. Figures 2a and 2b show emission spectra of naphthalene when excited in other vibronic bands of the $S_2 \leftarrow S_0$ electronic transition ($\lambda_{\rm exc} = 274.7$ and 268 nm respectively). Clearly the emission spectra of naphthalene excited to higher vibronic states in its second excited state S_2 are very similar to the spectrum obtained at the origin of the $S_2 \leftarrow S_0$ transition. They all present a maximum of emission around 350 nm. When the excitation energy increases (or $\lambda_{\rm exc}$ decreases), it is observed that the fine structure disappears and the fluorescence spectrum becomes diffuse, due to a fast intramolecular vibrational redistribution within the S_1 state, which is populated by internal conversion from the initially excited S_2 state.

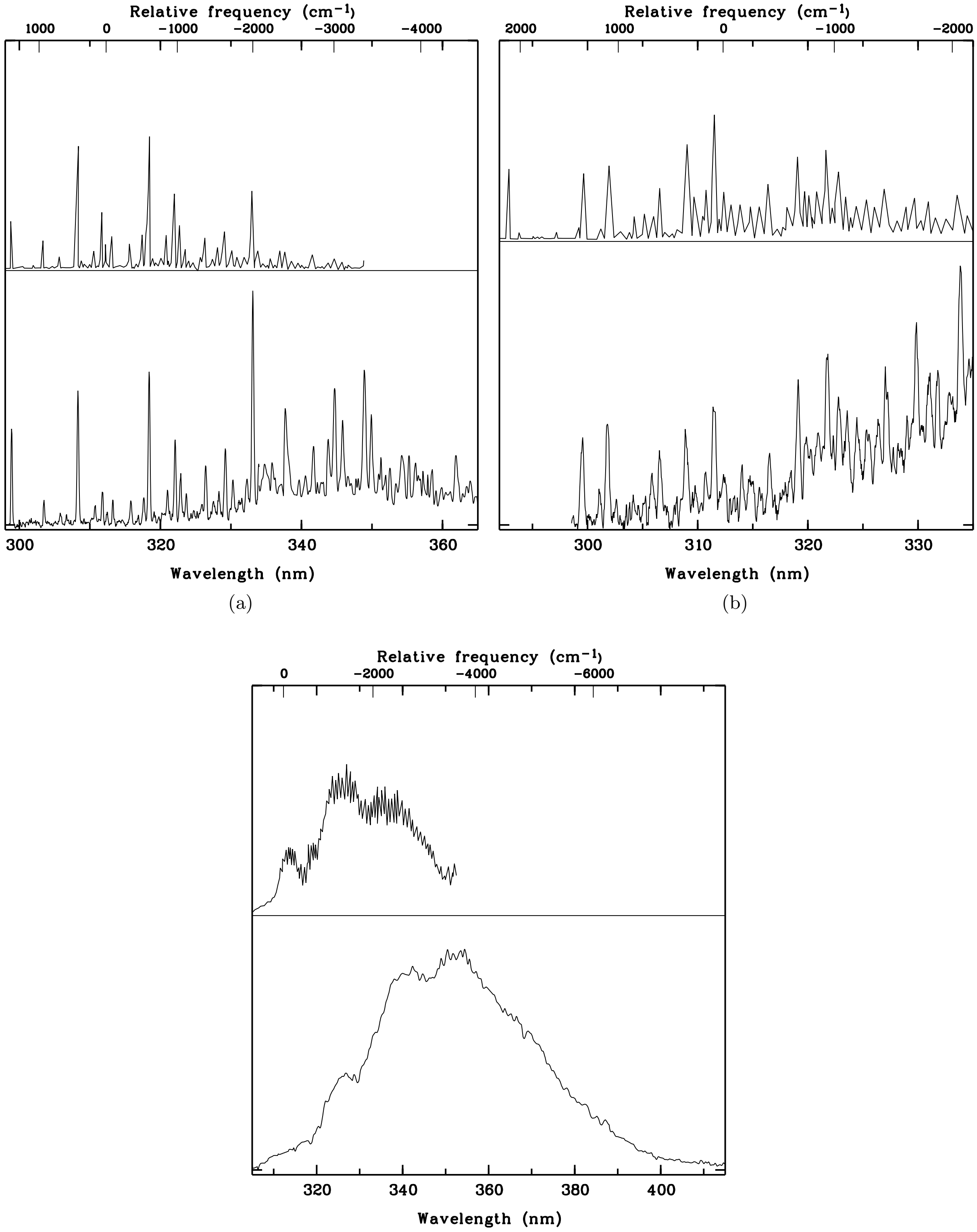
Table 1. Excitation wavelengths $\lambda_{\rm exc}$ and corresponding excitation energies above the S_1 origin at 32 020 cm^{-1} for which fluorescence emission spectra of naphthalene were obtained.

authors	excitation energy (cm^{-1})	$\lambda_{\rm exc}$ (nm)
Beck *et al.* (1981)	0	312.3
	435	308.2
	1422	299.0
	2122	292.9
	2570	289.1
	2867	286.6
	3068	285.0
	3797	279.2
	4029	277.4
Hermine (1994)	435	308.2
	5574	266.0
this work	1422	299.0
	2122	292.9
	2570[a]	289.1[a]
	3950	278.4
	4383	274.7
	5293	268.0

[a] Only the fluorescence decay has been recorded.

3.2 Fluorescence lifetimes and quantum yields

We measured the fluorescence lifetimes by recording the decay of the fluorescence signal emitted by naphthalene molecules, excited at the wavelengths $\lambda_{\rm exc} = 299$, 292.9, 289.1 nm (excitation above the S_1 origin but below the S_2 origin) and 274.7 nm (excitation above S_2). The measured signals exhibit a bi-exponential behavior with time, with a long component $\tau_{\rm l} \simeq 1$ μs and a short component 83 ns $< \tau_{\rm s} <$ 377 ns (Tab. 2). We deduced the fluorescence quantum yields $Q_{\rm fl} = \tau_{\rm s}/\tau_{\rm rad}$, where $\tau_{\rm rad}$ is the radiative lifetime of naphthalene, measured in supersonic jet by Behlen and Rice [11]: $\tau_{\rm rad} \simeq 1$ μs. We obtained the values $0.1 < Q_{\rm fl} < 0.45$ (Tab. 2). $Q_{\rm fl}$ was found to decrease when the excitation energy increases, as expected from the fact that the non radiative processes progressively prevail.

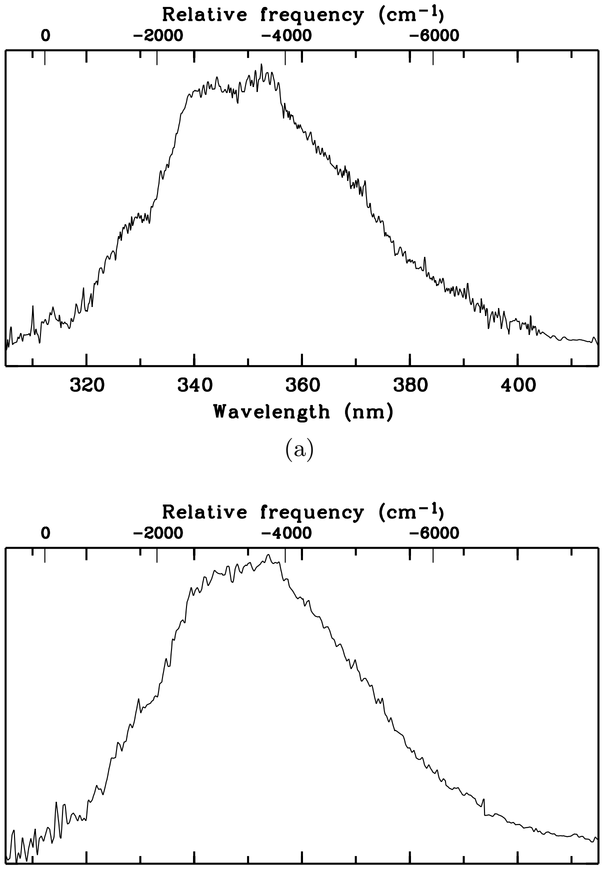


(a)

(b)

(c)

Fig. 1. Fluorescence emission spectra of naphthalene submitted to an excitation at the wavelengths λ_{exc}. (a) $\lambda_{\text{exc}} = 299$ nm, excitation energy = 1422 cm^{-1}; (b) $\lambda_{\text{exc}} = 292.9$ nm, excitation energy = 2122 cm^{-1}; (c) $\lambda_{\text{exc}} \simeq 279$ nm, excitation energy $\simeq 3900$ cm^{-1} ($\lambda_{\text{exc}} = 279.2$ nm for the upper spectrum, $\lambda_{\text{exc}} = 278.4$ nm for the lower spectrum). The upper spectra show Beck *et al.* [1] results. The lower spectra show our results. In all cases, spectra obtained by Beck *et al.* are weak towards the long wavelengths compared to our spectra.



(a)

(b)

Fig. 2. Fluorescence emission spectra of naphthalene induced by excitations at the wavelengths λ_{exc}. (a) $\lambda_{\text{exc}} = 274.7$ nm, excitation energy = 4383 cm^{-1}; (b) $\lambda_{\text{exc}} = 268$ nm, excitation energy = 5293 cm^{-1}. The maximum of emission is around 350 nm and the spectra are similar to the one obtained with $\lambda_{\text{exc}} = 278.4$ nm at the origin of the $S_2 \leftarrow S_0$ electronic transition (lower spectrum in Fig. 1c). The fine structures in the spectrum disappear when the excitation energy increases (or λ_{exc} decreases).

Table 2. Fluorescence lifetimes and fluorescence quantum yields of gas phase naphthalene molecules excited at different wavelengths λ_{exc} or with different excitation energies above the S_1 origin at 32 020 cm^{-1}. The fluorescence decay is biexponential with a long component τ_{l} and a short component τ_{s}. The fluorescence quantum yields Q_{fl} are compared to the values measured by other authors.

λ_{exc} (nm)	exc. energy (cm^{-1})	τ_{l} (μs)	τ_{s} (ns)	Q_{fl} (%) this work	*a*	*b*
299	1422	1.3	377	45	33	2
292.9	2122	1.8	116	12	16	2
289.1	2570	0.9	83	10	14	4
274.7	4383	1.0	83	10	—	7.5

[a] Stockburger *et al.* (1975)

[b] Suto *et al.* (1992)

4 Comparison to previous experiments

4.1 Fluorescence emission spectra

Previous studies of jet-cooled naphthalene in emission have been conducted by several groups, we focus here on the most extensive one by Beck *et al.* [1]. They obtained emission spectra when exciting the molecule at wavelengths between $\lambda_{\text{exc}} = 312.3$ nm (excitation at the origin of the $S_1 \leftarrow S_0$ electronic transition) and $\lambda_{\text{exc}} = 277.4$ nm (excitation above the second electronic state S_2).On the other hand Hermine [2] obtained in our laboratory spectra when exciting at 308 nm (435 cm^{-1} above the S_1 origin) and at 266 nm (excitation above S_2). However, the spectra obtained by Beck *et al.* [1] have weaker intensities at greater wavelengths compared to spectra obtained by Hermine [2].

We compare our emission spectra of fluorescence induced by excitations at $\lambda_{\text{exc}} = 299.0$, 292.9 and 278.4 nm to those obtained by Beck *et al.* [1] with similar excitation conditions ($\lambda_{\text{exc}} = 299.0$, 292.9 and 279.2 nm). The spectra are shown in Figures 1a–1c, respectively. In all cases, our spectra (lower spectra) exhibit components at longer wavelengths that are very weak or inexistent in the spectra obtained by Beck *et al.* [1] (upper spectra). The detector used by Beck *et al.* [1] had a weaker sensitivity for the longer wavelengths than the one we used. We could explain the difference between our results and the ones of Beck *et al.* [1] in supposing that the latter authors did not take into account the decrease of the response function of their detection system at longer wavelengths.

4.2 Fluorescence quantum yields

Several authors measured the fluorescence quantum yield of gas phase naphthalene molecules [11–17]. However, the values obtained vary by a factor that ranges from two to several times ten from an author to another. The reasons for such variations – which are observed within the energy gap between the S_1 and S_2 states, range in which the dominant radiationless transition is intersystem crossing to the triplets manifold – have been widely debated [18]. Apart from experimental calibration problems, they include local enhancement of intersystem crossing due to accidental resonances in the Herzberg-Teller vibronic spin-orbit coupling with the second (T_2) or third (T_3) triplets, as well as rotational effects. Here we compare our results to those obtained by Stockburger *et al.* [15] and more recently by Suto *et al.* [17] with the same excitation conditions. The values are given in Table 2. Our values are consistent with the values obtained by Stockburger *et al.* [15] and by Suto *et al.* [17] when considering the range where the molecule is excited to its second electronic state S_2 ($\lambda_{\text{exc}} < 280$ nm). Indeed this range will be dominant for the efficiency of the solar excitation. The values obtained by Suto *et al.* [17] when exciting the molecule to its first electronic state S_1 are much lower, and they surprisingly observe a fall when the excitation wavelength increases ($\lambda_{\mathrm{exc}} > 280$ nm) whereas the non radiative processes are expected to be less important. However it should be noted that they worked in conditions of a heated gas in which phenomena like rotational effects and molecular collisions are not negligible. On the other hand, our values are also consistent with the general trend in the quantum yields reported by Behlen and Rice [11].

5 Astrophysical simulation and implications

Spectroscopic data obtained with the three-channel spectrometer (TKS) of the spacecraft Vega 2, during the encounter with Comet P/Halley in 1986, show a broad band emissive feature between 342 and 375 nm. A laser-induced fluorescence experiment was conducted in the laboratory to record the dispersed emission spectrum of phenanthrene under jet-cooled conditions. A good agreement was obtained between the cometary and laboratory spectra, for both the wavelength positions of the main peaks and their relative intensities [9].

The chemistry able to produce a molecule such as phenanthrene is likely to create, under similar conditions, a whole family of PAHs. The detection of phenanthrene in Comet P/Halley implies that other PAHs could also be present in the comet and give rise to characteristic emission spectra. This point is in good agreement with the results provided by the IKS infrared spectrometer on Vega 2 that tend to show that at least one part of the infrared signature observed between 3.2 and 3.5 μm can be attributed to emission from PAHs when the ν_{CH} modes are excited [7]. The identification of PAHs in Comet P/Halley emphasizes the similarities between the material released by comets and diffuse interstellar nebulae. It adds a strong argument in favor of the fact that comets could consist of interstellar material.

In the present work, the laboratory conditions adequately reproduce the cometary situation: low temperatures and collisionless environment. In order to compare our experimental emission spectra of naphthalene molecules obtained under monochromatic excitation to spectra of cometary molecules exposed to solar radiation, we synthesized a fluorescence spectrum of naphthalene induced by the solar radiation. The fluorescence in the coma depends on two parameters: the number of photons received by the molecules and the number of photons reemitted by the molecules after absorption. Both parameters are characteristic of the spectral band considered, and each spectral band (in absorption) produces a characteristic spectral distribution in emission. The first quantity is given by the solar flux F_{Sol}, the second by the fluorescence cross-section $\sigma_{\mathrm{fl}} = \sigma_{\mathrm{abs}} Q_{\mathrm{fl}}$, where σ_{abs} is the absorption cross-section and Q_{fl} is the fluorescence quantum yield. The synthetic spectrum (Fig. 3) is the sum of the laboratory spectra, weighted by the factor:

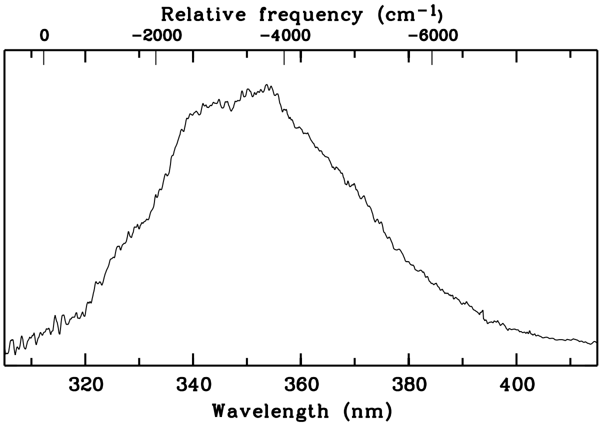


Fig. 3. Synthetic fluorescence spectrum of naphthalene submitted to the solar irradiation. The spectral resolution is 0.4 nm.

$$k(\lambda_{\mathrm{exc}}) = \int_{\Delta\lambda} \sigma_{\mathrm{abs}} Q_{\mathrm{fl}} F_{\mathrm{Sol}}\,\mathrm{d}\lambda$$

$\Delta\lambda$ is the wavelength interval for each absorption band centered on λ_{exc}.

The excitation spectrum obtained by Beck *et al.* [19] show that the fluorescence emission when exciting in the S_1 state is negligible compared to the emission when exciting in the S_2 state (considering integrated cross-sections). We used then the spectra that we obtained under excitation in the S_2 state to synthesize a spectrum. The solar fluxes F_{Sol} are given by Mount and Rottman [20], the absorption cross-sections σ_{abs} by Suto *et al.* [17] and the fluorescence quantum yields are deduced from our values and extrapolated at short wavelengths using the quantum yield curve reported by Suto *et al.* [17]. The synthetic spectrum consists mainly of a broad diffuse band centered at 350 nm. As already shown in Figure 1c, the fluorescence spectrum of naphthalene (lower spectrum) we obtained does not compare with the spectrum recorded by Beck *et al.* [1] (upper spectrum) and extends to much longer wavelengths, near 400 nm. As a consequence, the intense emission observed in the TKS spectra of Comet P/Halley at 323 nm cannot be considered as an unambiguous signature of naphthalene. This uncertain result does not rule out the fact that aromatic molecules signatures might be present in the TKS spectra, since small PAHs are efficient species for emitting fluorescence radiation in the near ultraviolet.

6 Conclusion

We obtained laser-induced fluorescence spectra of naphthalene molecules under laboratory conditions close to the cometary conditions (super-cooled gas phase molecules in a collision-free environment). We compared our spectra with previous spectra obtained under similar conditions by Beck *et al.* [1]. Our spectra extend to much longer wavelengths, up to 400 nm.

We also measured the fluorescence lifetimes and deduced the values $10\% < Q_{\text{fl}} < 45\%$ for the fluorescence quantum yields of naphthalene excited with energies from 1422 cm^{-1} to 4383 cm^{-1} above the origin of the $S_1 \leftarrow S_0$ electronic transition.

We used our emission fluorescence spectra of naphthalene excited by monochromatic lasers to synthesize a fluorescence spectrum with excitation conditions that reasonably well simulate the radiation field in the coma of a comet. We compared then this synthetic spectrum with the near ultraviolet spectra of Comet P/Halley taken by the TKS spectrometer on Vega 2 spacecraft. Contrarily to what was expected when using the results by Beck *et al.* [1], the naphthalene does not appear as a possible carrier of the emission feature centered at 323 nm that arises in TKS spectra taken at distances close to the nucleus (within 3000 kilometres). At that point, the 323 nm feature still remains unidentified. This feature was probably detected by Valk *et al.* [21] who reported the presence of two unidentified lines at 321.9 and 323.2 nm in spectra of Comet Austin 1989cl.

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