

DETECTION OF ANTHRACENE IN THE UV SPECTRUM OF COMET 1P/HALLEY

Moreels, G.¹, Clairemidi, J.¹, Mousis, O.¹ and Bréchnac, P.²

Abstract. Following the detection of three small PAHs, naphthalene, phenanthrene and pyrene in dust grains collected by the Stardust probe in the environment of Comet 81P/Wild 2, we reprocessed the UV spectra of Comet 1P/Halley recorded by the Vega-TKS spectrometer. The near-UV cometary spectra were compared with laboratory spectra of anthracene obtained under laser-induced fluorescence conditions. Four main peaks coincide at 362, 367.5, 373 and 382.5 nm. This shows that anthracene is present in the innermost coma of Comet 1P/Halley and comes in addition to the previous detection of phenanthrene and pyrene.

1 Introduction

Naphthalene, phenanthrene and pyrene were recently identified in comet 81P/Wild2 samples collected during the Stardust mission (Sandford et al. 2006; Clemett et al. 2007). In addition, by using a model for the infrared emission of dust based on a statistical mix of PAHs with an average size $\sim 1 \text{ \AA}$ for pyrene (Li & Draine 2001), Lisse et al. (2006) also detected infrared signatures of PAHs at 6.2 and 7.6 μm in Spitzer spectra of comet 9P/Tempel 1 ejecta. These new findings led us to re-investigate the UV part of TKS spectra in order to search for new fluorescence bands of PAHs, as these compounds are quite efficient in emitting near UV and blue luminescence when exposed to UV radiation. In this paper, we present a set of four spectra of the inner coma of comet 1P/Halley, each one being an average of four individual spectra taken at different projected distances between 421 and 932 km from the nuclei. The data are compared with a fluorescence spectrum of anthracene obtained in the laboratory under simulated cometary conditions. Both types of spectra, cometary and laboratory, present comparable features that allow a confident identification of anthracene in 1P/Halley.

2 Spectra of Halley's inner coma

Spectra of Halley's inner coma in the near UV were obtained on March 9, 1986 with the TKS spectrometer onboard the Vega2 spacecraft. In the inner coma at $p \leq 3000$ km, during the approach and encounter period, intense fluorescence broad band emissions (10–50 kRayleighs / nm) gradually emerged as the spacecraft approached the comet. The spectra recorded during this session exhibit a noticeable variability which reflects the inhomogeneities of the cometary medium close to the nucleus. A selection of them is displayed in Fig. 1, where a number of fluorescence bands are seen in the 340–390 nm spectral range.

Polyatomic molecules which emit fluorescence radiation in the near UV are numerous. Our search was oriented towards methanol and formaldehyde, since these molecules have been detected in several comets, and towards PAHs which present fluorescence bands in the UV and visible. In the UV, methanol in the gaseous phase shows a weak absorption band at $\lambda \sim 180\text{--}200$ nm. The molecule is dissociated and produces mainly formaldehyde or, with a lower rate, methoxy radicals. At shorter wavelengths, $\lambda < 150$ nm, the dissociation products are methyl and OH ($^2\Sigma$) radicals. As a result, methanol does not seem to be a possible fluorescence carrier of the observed emission. In the case of formaldehyde, its fluorescence spectrum presents ten regularly spaced bands but none of them coincide with the reported emission features between 358 and 385 nm.

Among the large family of PAHs, we identified phenanthrene (Moreels et al. 1994) and pyrene (Clairemidi et al. 2004) from TKS spectra of Halley's inner coma. These two PAHs were also identified in the samples of

¹ Observatoire de Besançon, Institut UTINAM, CNRS-UMR 6213, BP 1615, 25010 Besançon Cedex, France; guy.moreels@obs-besancon.fr

² Laboratoire de Photophysique Moléculaire, CNRS, Univ. Paris-Sud, Bât. 210, 91405 Orsay Cedex, France

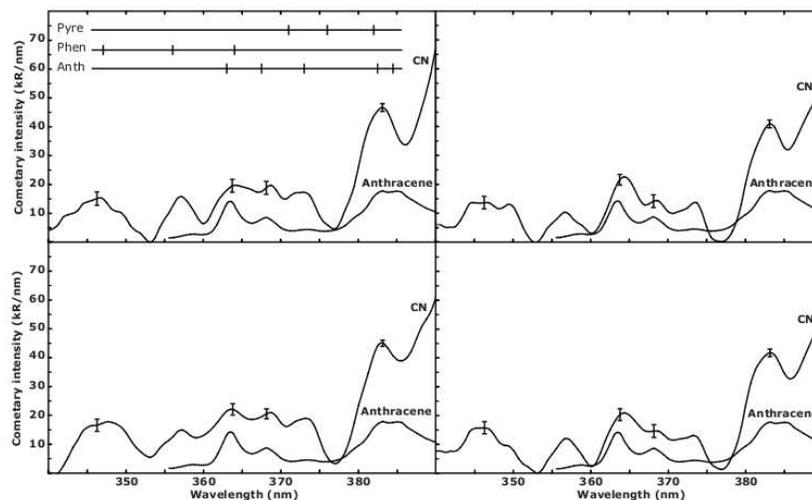


Fig. 1. Comparison of cometary spectra with the laboratory spectrum of anthracene. The CN emission band is not subtracted from the cometary spectrum. The laboratory spectrum of anthracene, shown with arbitrary intensity units, is presented below the cometary spectrum. The cometary spectrum shown in each panel is an average of four different individual spectra taken at different projected distances p between 421 and 932 km. Four main peaks coincide at 363, 367.5, 373 and 382.5 nm. Error bars are plotted at the wavelengths of several PAHs emission bands. Marks in the upper left panel denote the location of the anthracene, phenanthrene and pyrene features.

the comet 81P/Wild 2 collected by Stardust (Sandford et al. 2006; Clemett et al. 2007), and presented as a good match to the material excavated by the Deep Impact experiment from comet 9P/Tempel 1, as observed by the Spitzer Space Telescope at 5–35 μm (Lisse et al. 2006). PAHs are considered to be the best candidates as possible carriers of the cometary emission, because their fluorescence bands are expected to be located in the 330–385 nm spectral range.

3 Identification of Anthracene

The identification of some of these bands in comet 1P/Halley as being anthracene has been done on the basis of comparisons between the cometary spectra and emission spectra obtained in the laboratory, under conditions which provide valuable simulation of the astrophysical situation, i.e. super-cooled gas phase molecules in a collision-free regime. The experimental conditions are described in Hermine (1994), Moreels et al. (1994) and Clairemidi et al. (2004). The characteristics of the experiment (very low temperature and absence of collisions) provide an appropriate simulation of the cometary conditions. The fluorescence spectra correspond to the recording of the dispersed emission resulting from excitation at a fixed laser wavelength.

The photophysical properties of the anthracene molecule must be invoked in order to derive from experimental data the expected emission spectrum of the molecule if present in the cometary environment. This is done with the help of the diagrams presented in Fig. 2. The central part of the figure is an energy levels scheme following partly the traditional Jablonski's representation. The fluorescence excitation spectrum of jet-cooled anthracene is reported on the left hand side of the figure, while the standard solar spectrum is recalled on the right hand side. The central scheme consists of three piles of vibrational energy levels built above the vibrationless electronic singlet states: the ground state S_0 (right), the first excited singlet S_1 (middle), and the fourth excited singlet S_4 (left). Note that the second and third excited singlet states are not represented since, as apparent from the fluorescence excitation spectrum (left), the $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions have negligible oscillator strengths. The metastable triplet states are not shown either, although they contribute to the reduction of the fluorescence quantum yield by inter-system crossing non radiative transitions. It thus appears that only the vibronic bands belonging to the $S_1 \leftarrow S_0$ and $S_4 \leftarrow S_0$ electronic transitions are efficient to excite the fluorescence of anthracene. Excitation of the S_4 state is immediately followed by fast non radiative transitions of internal conversion to the S_1 state (wavy horizontal arrow in the figure), as evidenced by the fact that the fluorescence is emitted in the wavelength range of the $S_1 \leftarrow S_0$ transition.

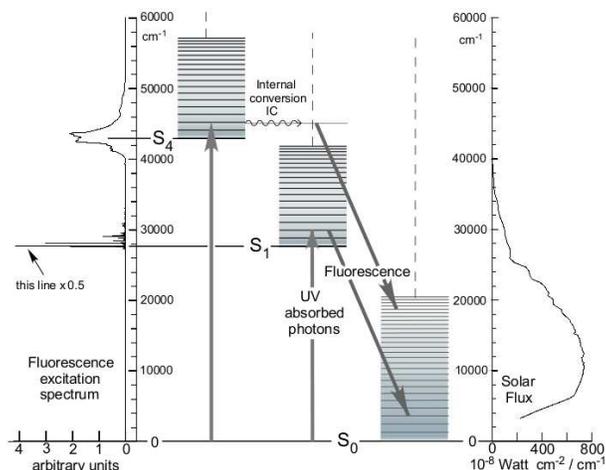


Fig. 2. Energy levels diagram showing the allowed electronic transitions within the singlet states of anthracene. On the left hand side, the fluorescence excitation spectrum of the jet-cooled molecules is reproduced (Hermine 1994). On the right hand side, the solar spectrum is shown for comparison. Note that the S_2 and S_3 states are not represented since they do not contribute to the excitation because of their very low oscillator strengths. Triplets which contribute to the reduction of the fluorescence quantum yield by non-radiative transitions are not shown for overall clarity.

The experimental study shows that excitation through the various vibronic bands of the $S_1 \leftarrow S_0$ transition gives rise to a dispersed emission spectrum which is red-shifted relative to the origin transition at 361 nm, always similar when the excitation wavelength is varied and which evolves towards an essentially stable spectrum when intramolecular vibrational redistribution (IVR) is established (Bréchnignac & Hermine 1994). It is clear from the solar spectrum in Fig. 2 that the flux available for excitation to S_4 is significantly smaller than it is for excitation to S_1 . Interestingly enough the quantum yield is also reduced from 0.67 (at the origin of S_1) to 0.02 (at the high energy side of the S_4 band). Consequently, the contribution of the fluorescence from S_1 is expected to be about 20 times larger than that from S_4 . The laboratory photophysical studies thus led us to adopt as expected cometary spectrum the spectrum with $\lambda_{exc} = 344$ nm reported by Lambert et al (1984), which is reproduced in the four panels of Fig. 1.

We selected for this figure cometary spectra where the fluorescence bands of anthracene at 363, 367.5, 373, 382.5 and 384.5 nm are present. As the medium probably contains a mixture of PAHs, the simultaneous presence in the four spectra of the fluorescence bands of anthracene at 363, 367.5, 382.5–384.5 nm constitutes a strong criterion for identifying this molecule. The main fluorescence bands of phenanthrene located at 347, 356, 364 nm are also seen. In the case of pyrene, the bands located at 371, 376 and 382 nm are hardly seen in the spectra that were chosen in the present work. As a result, the spectra shown in Fig. 1 suggest the identification of anthracene in Halley's comet but also confirm the presence of phenanthrene.

Following the same approach as in our previous cometary PAHs works (Moreels et al. 1994; Bréchnignac & Hermine 1994, Clairemidi et al. 2004), i.e. relying on the absolute oscillator strength for $S_1 \leftarrow S_0$ absorption and fluorescence quantum yields from S_1 (near $\lambda_{exc} = 344$ nm, $Q \simeq 0.2$) (Hermine 1994), integrating the cometary intensity in anthracene bands (from Fig.1) and assuming the expansion velocity is 1 km/s, it is possible to derive the production rate of anthracene: $Q_{anthracene} \sim 10^{26}$ molecules s^{-1} .

This value may be compared with the production rate of C_2 , estimated to be 6×10^{27} molecules s^{-1} for March 9, the encounter day (Krasnopolsky et al. 1986). Comparing the production rate of anthracene to the estimated production rate of water mentioned by Krasnopolsky et al. (1986), $Q_{H_2O} = 2 \times 10^{30}$ molecules s^{-1} , and by Encrenaz et al. (1988) for P/Halley, $Q_{H_2O} = 10^{30}$ molecules s^{-1} , we derive a maximum abundance of anthracene relative to water of 5×10^{-5} to 1×10^{-4} . Note that Bockelée-Morvan et al. (1995) found a lower PAH abundance relative to water ($\sim 1.5 \times 10^{-6}$ to 10^{-5}) in a set of seven comets, but their derived abundances depend on modeling assumptions which are still uncertain and there is a significant diversity among comets, namely in the dust/gas ratio and in the composition of the coma.

In the same conditions the cometary intensity in phenanthrene bands from Fig. 1 would lead to $Q_{phenanthrene}$ ranging from 6×10^{26} to 10^{27} molecules/s. The order of magnitude is similar to our previous determination

(Moreels et al. 1994) although weaker by a factor of $\simeq 2$. Such a difference can be explained by the fact that the spectra in Fig. 1 have been selected to clearly show up the anthracene bands, in contrast to our previous work. The higher abundance of phenanthrene compared to anthracene could be explained by the fact that it is more stable than anthracene (see e.g. Fig. 2 p.4, Bjørseth 1983).

This reveals a clear variability in the spectra which must have its origin in the heterogeneity of the material composition along the time-varying line-of-sight. Such a behavior is fully consistent with the evidence of highly anisotropic jets in Halley's coma, and is expected to be emphasized if the PAHs molecules are indeed outgassed from the dust particles themselves, possibly released by the fragmentation of clumps. Such a process is also proposed by Green et al. (2007) to explain the impact counts data recorded in the Wild 2 coma during the Stardust closest approach.

4 Summary and discussion

The recent identification of PAHs in the cometary dust grains collected during the Stardust mission (Clemett et al. 2007) led us to re-investigate the spectra of Halley's inner coma recorded by the TKS spectrometer. We compared the cometary data with laser induced fluorescence spectra obtained under cooled molecular jet conditions. Using anthracene vapour, four main peaks located at 363, 367.5, 373 and 382.5 nm were identified in the laboratory spectrum of the 3-ring PAH, as well as in the cometary spectra. In addition, the spatial distribution of the emission exhibits a p^{-1} variation which shows that its carrier, anthracene, is emitted by the nucleus or by dust packs in the coma. The identification of anthracene confirms the previously reported detection of phenanthrene (Moreels et al. 1994), and pyrene (Clairemidi et al. 2004). It should be noted that the structure of individual spectra is not uniform for the whole set of TKS data. This reveals some heterogeneity in the composition of clumps or of dust grains as pointed by the Stardust results (Clemett et al. 2007). The chemistry capable of producing such PAHs is likely to create, under similar conditions, a whole family of polycyclic aromatic molecules. In particular, the presence of naphthalene is not excluded from our spectra but difficult to determine definitely because the expected spectrum presents only one broad (~ 25 nm) band without characteristic features (Bréchnignac & Hermine 1994). These detections imply that other PAHs might also be present in comet Halley and give rise to characteristic emission spectra.

References

- Bjørseth A., 1983, Handbook of polycyclic aromatic hydrocarbons, Marcel Dekker, INC. (New York 10016)
- Bockelée-Morvan D., Brooke T. Y., Crovisier J., 1995, Icarus, 116, 18
- Bréchnignac P., Hermine P., 1994, in A.I.P. Conf. Proc. 312, Molecules and Grains in Space, ed. I. Nenner (New York: AIP), 613
- Clairemidi J., Bréchnignac P., Moreels G., Pautet D., 2004, P&SS, 52, 761
- Clemett S. J., Nakamura-Messenger K., McKay D. S., Sandford S. A., 2007, LPI, 38, 2091
- Encrenaz T., D'Hendecourt L., Puget J. L., 1988, A&A, 207, 162
- Green S. F., et al., 2007, ESASP, 643, 35
- Hermine P., 1994, PhD, Université Paris XI, Orsay
- Krasnopolsky V. A., et al., 1986, Nature, 321, 269
- Lambert W.R, Felker P.M., Zewail A.H., 1984b, J. Chem. Phys. 81, 2217
- Li A., Draine B. T., 2001, ApJ, 554, 778
- Lisse C. M., et al., 2006, Science, 313, 635
- Moreels G., Clairemidi J., Hermine P., Bréchnignac P., Rousselot P., 1994, A&A, 282, 643
- Sandford S. A., et al., 2006, Science, 314, 1720