

## Frozen Hydrocarbon Particles of Cometary Halos as Carriers of Unidentified Emissions

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**Abstract.** The possible nature of unidentified cometary emissions is under discussion. We propose a new model of the ice particles in cometary halos as a mixture of frozen polycyclic aromatic hydrocarbons and acyclic hydrocarbons. We describe principal properties of frozen hydrocarbon particles (FHPs) and suggest interpreting some of the unidentified cometary emission lines as the photoluminescence of FHPs. The results of comparative analysis are present.

**Key words.** Comet—ice—luminescence—frozen hydrocarbon particles—unidentified lines.

### 1. Introduction

The problem of unidentified cometary emissions in optical part of a cometary spectrum is known to remain of great interest. Such emissions are unidentifiable both numerically and comparatively, and are usually presented in the form of tables or data base (Brown *et al.* 1996; Cochran & Cochran 2002). Their identification depends on the methods used to obtain and process the spectral data, the amount of accumulated comparative laboratory results, knowledge of other excitation mechanisms for the corresponding emission lines. Although unidentified emissions may emerge within an ordinary resonance–fluorescence mechanism due to transition of corresponding atoms and molecules from higher levels, there still remains a possibility of photoluminescence excited in a solid cometary substance exposed to solar UV radiation (Simonia 1999). This process appears to be highly probable, particularly, if we take into account considerable amount of organic components in the cometary ice. Polycyclic Aromatic Hydrocarbons (PAHs) belong to a most important class of chemical compounds found in cosmic bodies. There is no doubt that they are contained in the cometary substance (Ehrenfreund *et al.* 2000). We suggest that ice of a cometary nucleus may contain mixtures of PAHs and acyclic hydrocarbons, consequently, the icy particles of the cometary halo may fully consist of such solid mixture or, at least, contain a significant amount of it. Solar UV radiation can excite photoluminescence of icy particles in the halo. A low albedo of the particles, consisting of those mixtures and a high quantum yield of photoluminescence for PAHs ensure detectability of corresponding luminescence emissions.

PAHs and acyclic hydrocarbons, as well as other possible components, remain frozen at low temperatures, and can be therefore named Frozen Hydrocarbon Particles (FHPs).

## 2. FHPs as carriers of unidentified cometary emissions

Quantum yield of luminescence for many organic compounds is about to d'Hendecourt *et al.* (1986) stated that the quantum yield for PAHs molecule may be about 50%. According to Gudipati *et al.* (2003) the quantum yield varies from 90 to 100% for smaller grains containing frozen organic mixtures.

The above facts are evidence that, when exposed to UV radiation, frozen organic mixtures have highly efficient, bright luminescence. The cometary nuclear ice may contain mixtures of frozen PAHs and acyclic hydrocarbons, and the mixtures are supposed to appear as a solid solution of the "solvent-substance" type, where the PAHs make the "substance" and the acyclic hydrocarbons are the "solvents". It actually means that PAHs dissolved in acyclic hydrocarbons make a solid solution. The optical properties of such a frozen substance, i.e., polycrystalline solution, depend on the properties of the solvent, solution crystallization conditions, presence of a luminescent component, a luminogen, relation between the components of the solution and the composition of admixtures in the solution.

Presence of such polycrystalline solutions in the cometary ice is rather probable. The surface layers of an icy cometary nucleus are the sources of heterodispersive frozen hydrocarbon particles, ejected and carried into the circumnuclear area while the heliocentric distance of the comet diminishes. These icy particles of different sizes and irregular symmetry will form an icy halo at corresponding heliocentric distances. We believe that the size of an individual FHP may vary from microns to millimeters. FHPs will have a specific colour characterizing frozen PAHs+acyclic hydrocarbons mixture. With low concentrations of admixtures, FHPs should appear as gray icy particles. So, cometary nuclei can be surrounded by a halo of an FHP layer. In natural conditions, in addition to FHPs, a halo may contain silicate dust and finely dispersive carbonaceous particles. Exposed to solar UV radiation, FHPs produce intensive luminescence within 3800–6700 Å. Other components of halo, such as inorganic dust particles, will also luminesce, though with low quantum yield. FHP luminescence spectrum depends on the chemical composition of a particular mixture, PAH concentration in the polycrystalline solution, admixtures, if there are any, temperature and, occasionally, size of the icy particles, solar activity phase and some other factors, among which the chemical composition and temperature of a particular FHP are the most important.

When exposed to solar UV-radiation, FHPs of different chemical compositions and temperatures will produce luminescence of different spectral compositions. Pringsheim *et al.* (1951) noted that at 54.3 K (temperature of liquid oxygen), diffuse spectral bands of many crystalline organic compounds resolve into groups of narrow bands or lines. This is particularly significant for FHPs and suggests of, at least, two types of luminescence spectra of the cometary halo icy particles: (a) spectra with wide diffuse bands, and (b) spectra in the form of a series of narrow lines or bands.

Let us now dwell on some properties of FHPs in a 60–85 K temperature range, referring to laboratory data of FHP substance analogs. Teplitskaya *et al.* (1978) obtained polycrystalline solutions of the above described composition to study PAH luminescence at 77 K, and found normal paraffins to be the best solvent in producing PAH

discrete luminescence and absorption spectra. In the case of compounds with a linear structure (polyacene, polyphenyl, diphenylpolyene, etc.) the sharpest spectra were observed with the linear dimensions of the solvent molecules close to those of the PAH molecules.

Experimental excitation of an aromatic hydrocarbon solution with laser light in (0–0) band at  $T = 4.2$  K produced high-structure hydrocarbon spectra with the line width of 0.15–0.47 Å. This is true for majority of the solvents that crystallize and glassify while freezing, remaining chemically neutral to the molecules solved therein, and optically transparent in the absorption and emission areas of PAH molecules. Experiments also demonstrated that at low PAH concentrations in some solutions, the mixture luminescence spectrum consists of a band series, while at higher PAH concentrations a series of narrow lines may form. Luminescence spectrum of pyrene at its concentration  $10^{-4} \text{ mol} \cdot \ell^{-1}$  in *n*-pentane did not reveal a narrow line. Shpol'skii (1962) proved that when PAHs were dissolved in special solutions – hydrocarbons (e.g., in *n*-pentane) at 77 K and lower temperatures, the resulting frozen mixture produced a luminescence spectrum of a series of numerous very narrow lines. Such spectra are called luminescence quasilinear spectra. Position in the band length scale, relative spacing and relative intensity of the lines are fairly specific for each molecular structure, indicating normal electronic-vibrational state of the corresponding molecular structures. We suppose that FHPs cometary halos which are chemically identical to their laboratory analogs, also produce quasilinear luminescence spectra when exposed to UV radiation.

It is noteworthy, however, that FHP quasilinear luminescence spectra produced in a natural cosmic environment may differ from laboratory results due to specific cometary coma temperature and pressure, bombardment with charged particles, or collisions with gaseous neutrals of cometary atmosphere. The width of each FHP luminescence spectral line seems to depend on the heliocentric distance, since the cometary substance temperature changes with the distance from the sun. Lines of quasilinear luminescence spectra of FHP may demonstrate widening at the substance temperature  $T > 85$  K and low PAH concentrations. Gradual widening of the lines in the icy particle luminescence spectra may proceed with a diminishing heliocentric distance, as the FHP volatile component gets exhausted. Thus, if the FHP substance consists of PAHs+*n*-hexane, the depletion process starts as soon as the icy particle's temperature reaches  $T \approx 290$  K, at which point the *n*-hexane begins to evaporate vigorously. This will naturally change the luminescence spectrum of respective FHPs. Consequently, FHPs can form as sources of short-term luminescence. Such short-lived emissions are not infrequent in cometary spectra and are often unidentifiable. So, the FHP luminescence spectrum for cometary halo depends on:

- the chemical composition of the frozen mixture,
- PAH concentrations,
- heliocentric distance,
- dynamic properties of the halo.

One should also notice the role of the exciting radiation since its range and intensity are considerably different from laboratory ones. The icy particles in the halo are exposed to a short-wave solar radiation of a fairly wide range, and fluxes of charged particles of the solar wind.

Photoprocessing of FHPs exposed to solar UV radiation affects the FHP luminescence spectrum, changing its composition as well as distribution of the luminescence emission intensities in the series. It is worth-while mentioning that those changes occur during a certain time interval that could be defined as an FHP photoprocessing period, which may vary from a few hundred seconds to a few years for each class of FHPs at different heliocentric distances.

The whole picture appears to be complicated, changeable, dependent on the icy particle temperature, PAH concentration and composition, exciting radiation composition. Nevertheless similar photoluminescence emissions are certain to be recorded from different comets at the same heliocentric distances (e.g.,  $r = 1$  a.u.) with assumed chemical identity of the halo icy particles. So, spectra of different comets may demonstrate similar emissions that have so far been considered unidentifiable.

We suggest interpreting some of the unidentified emission lines in cometary spectra as the photoluminescence of FHPs. We performed calculations of the ratio of the photoluminescence flux to the scattered solar radiation flux  $Flum/Fscat$  for typical conditions of actual cometary halos composed of millimeter-size FHPs. The calculation was performed on the following conditions: the FHP is composed of phenanthrene  $C_{14}H_{10}+n$ -hexane at  $T = 77$  K, and the phosphorescence line is  $L = 4602 \text{ \AA}$  (Teplitskaya *et al.* 1978). We considered an FHP that scattered solar radiation with a wavelength of  $L = 4602.17 \text{ \AA}$ . According to Cochran *et al.* (2002) in the spectrum of comet 122P/de Vico was observed unidentified emission at  $\lambda = 4602.17 \text{ \AA}$ . Subsequent calculations were performed using Plank's formula and an expression for energy exposure  $E = (w/s)/r^2$  (Simonia *et al.* 2003) with  $w = F \cdot t$  (flux and time) where  $w$  is the total energy emitted at a corresponding wavelength,  $s$  is the halo's surface area with radius  $R = 500$  km,  $r$  is the heliocentric distance (1 a.u.). The assumed FHP luminescence quantum yield was 50%, the FHP albedo  $A = 0.1$ , the exciting UV solar radiation wavelength was  $2930.25 \text{ \AA}$  (phenanthrene absorption area). We found  $Flum/Fscat = 2.344$ , which proves that the luminescence signal lies above the scattered solar continuum and is a weak but quite recordable emission. Such relatively weak unidentified emissions are widely encountered in the atlas by Cochran *et al.* (2002). (The error of  $\pm 0.17 \text{ \AA}$  is negligible, particularly in view of the above described widening of the corresponding lines.) A high quantum yield of the PAH luminescence and application of fast instrument and high resolution spectrographs ensure that the luminescent signal is recognizable. We calculated also  $Flum/Fscat$  ratios for other emissions for the same comet. We obtained similar results  $Flum/Fscat > 1$ .

We compared laboratory luminescence spectra of FHP substance analogs with the observed cometary spectrum containing a set of unidentified emissions. We used an atlas of quasi-line luminescence spectra for aromatic molecules (Teplitskaya *et al.* 1978) as the laboratory data base and a High Resolution Atlas of Comet 122P/de Vico (Cochran & Cochran 2002) as the observation data. The results were summed up in a table, a column of the table lists the PAH descriptions and formulas, b column gives the solvent, c column the luminescence emission wavelengths for polycrystalline solutions and d column cites the unidentified cometary emission wavelengths from de Vico spectrum. The allowed error of the analysis was  $\pm 1 \text{ \AA}$ .

a	b	c	d	
Pyrene C16H10	<i>n</i> -hexane	3929	3929.28	
		5894	5893.85	
		6027	6026.66	
		6036	6036.42	
		6346	6346.78	
		6413	6413.07	
1,2-3,4 dibenzanthracene C22H14	<i>n</i> -octane	3862	3862.07	
		3936	3936.23	
		3949	3949.15	
		4069	4069.03	
	<i>n</i> -hexane	4091	4090.99	
		3934	3934.90	
		3955	3955.13	
		3981	3981.64	
		4055	4054.64	
		4067	4067.35	
Anthracene C14H10	<i>n</i> -hexane	3950	3950.02	
		3963	3963.11	
		3985	3985.44	
		4011	4011.44	
		4023	4023.07	
		4075	4075.98	
		4248	4248.06	
		4264	4263.07	
		4292	4291.73	
		4490	4489.90	
		4519	4519.09	
		<i>n</i> -heptane	3867	3867.16
			3967	3967.51
			3987	3987.26
			4002	4001.97
			4025	4024.93
			4064	4064.46
		4094	4093.94	
4295	4294.88			
4541	4540.82			
4573	4572.97			
Diphenyl C12H10	<i>n</i> -hexane	4371	4371.16	
		4570	4570.12	
Fluorene C13H10	<i>n</i> -hexane	4239	4238.71	
		4525	4525.13	
		4552	4552.25	
Phenanthrene C14H10	<i>n</i> -hexane	4591	4591.28	
		4602	4602.17	
		4957	4957.43	
		4991	4991.97	
		5060	5060.23	
		5313	5313.29	
		5327	5327.89	
5400	5400.20			
Chrysene C18H12	<i>n</i> -hexane	4000	4000.09	
		4983	4982.63	
		5028	5028.42	
		5058	5057.71	

a	b	c	d
		5318	5318.08
		5352	5352.12
		5422	5422.38
		5510	5509.39
Coronene C <sub>24</sub> H <sub>12</sub>	<i>n</i> -hexane	4330	4329.69
		4434	4433.11
		4451	4451.59
		4536	4536.33
		4543	4543.00
		4550	4549.99
		5159	5159.89
		5260	5260.31
		5510	5509.39
		5615	5615.23
		5630	5629.74
		5930	5929.59
Tetracene C <sub>18</sub> H <sub>12</sub>	<i>n</i> -hexane	4751	4750.96
		5087	5086.61
		5238	5237.57
	<i>n</i> -nonane	4719	4719.17
		4794	4794.01
		4866	4866.26
		5135	5135.96
		5176	5176.26
		5197	5197.21
		5219	5218.65

Described FHP concept and the comparative analysis of the observation with laboratory data summed up in the above table suggest that an FHP of the ice halo of de Vico comet may comprise, as its basic mixture, few aromatic hydrocarbons producing a polycrystalline solution with a number of acyclic hydrocarbons. It is only natural for an FHP to contain small amounts of admixtures. In fact, de Vico's icy halo can be a set of FHPs of various chemical compositions. A cloud of heterodispersive frozen hydrocarbon particles of different chemical compositions exposed to solar UV radiation produces luminescence emissions within a wide range of 3800–6700 Å. Our comparisons involved laboratory data on hydrocarbon fluorescence and phosphorescence. Polycrystalline solutions – chemical analogs of the FHP substance demonstrated in the laboratory intensive fluorescence and phosphorescence. In the natural cosmic environment with different excitation conditions, FHP of the cometary halo may have different afterglow periods, i.e., they may produce fluorescence or phosphorescence spectra. The laboratory base that was used in our comparative study contained 100 aromatic molecules. Occurrence of PAHs in comets was a subject of study for quite a few authors, for instance, Moreels *et al.* (1994) proved that the inner coma of comet P/Halley contains phenanthrene. They detected this aromatic hydrocarbon in the near UV range of the comet spectrum. They pointed out stability of PAHs in the cosmic environment and suggested possible relation between PAHs of the solar system bodies and PAHs of interstellar origin. According to Crovisier *et al.* (1999) the presence of PAHs in comets still remains doubtful. Ehrenfreund *et al.* (2000) mentioned detection of PAHs and aliphatic hydrocarbons in the cometary substance in the section “Cometary Dust and Refractory Organics” of their extensive review.

Aromatic hydrocarbons can be found in comets both in the condensed and gaseous phase. The above described FHPs of a corresponding chemical composition carry a number of photoluminescence emissions that have been so far considered as unidentified ones, although it is hardly possible that all the unidentified emissions are actually FHP photoluminescence. Other parts of unidentified emissions belong to resonance fluorescence of daughter molecules and ions. The Flum/Fscat ratio was calculated assuming the albedo value of 0.1.

### 3. Conclusion

The concept of FHPs has been suggested and basic features of their photoluminescence have been described. It was proposed to regard at least a part of the unidentified cometary emissions as FHP photoluminescence. A comparative analysis was carried out involving spectra of FHP's substance laboratory analogues with spectra of de Vico comet containing several thousands of unidentified cometary emissions, which demonstrated that the icy particles of that comet's halo may contain at least 9 aromatic molecules. This work is only the first step in this field of research, and our intention is to develop it further by updating our methods and results.

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