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DUST PLASMA ANALOGUE FOR INTERSTELLAR 217.5 nm EXTINCTION

I. Stefanović[1,2]

[1]*Institute for Experimental Physics II, Ruhr University Bochum 44781 Bochum, Germany*

[2]*Institute of Physics, Belgrade University, POB 68, 11080 Belgrade, Serbia*

E–mail: *ilija.stefanovic@rub.de*

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SUMMARY: The new ultraviolet (UV) extinction measurements of carbonaceous nanoparticles in the range from 140 nm to 260 nm are presented. The plasma polymerized hydrocarbon nanoparticles were already proposed as a new astro analogue, which describe the infrared (IR) extinction spectra in an excellent way. We use the same particles to find the possible carrier of the "mysterious" UV 217.5 nm extinction "bump" of interstellar media (ISM).

Key words. dust, extinction – Methods: laboratory

1. INTRODUCTION

The 217.5 nm bump is the dominant and most controversial feature on the interstellar extinction curve (Schnaiter et al. 1998, Chen et al. 2006, Sorrell 1990). The carrier of 217.5 nm extinction bump remains unidentified over 40 years after its first detection (Chen et al. 2006). It is speculated that its source is a carbonaceous component of ISM, especially a graphitic one. It has been attributed to p-electron plasmon absorption or π - π^* band transition in small graphite particles or amorphous carbon grains (Schnaiter et al. 1998). Despite of the early assignment to carbonaceous material, the question whether the 217.5 nm band is produced by carbon grains or by some other material is still lively topic of debate (Schnaiter et al. 1998, Chen et al. 2006, Sorrell 1990).

Role of the dust particles in planet formation, radiation conversion and as a source of biological material in space was largely discussed at length in the literature (Sandford 1996, Pendleton and Allamandola 2002). The dust plays a role of the necessary third collision partner in various molecular condensation reactions as well as in the reprocessing the UV radiation. New measurements of Titan aerosols have further increased the interest in dust (Waite et al. 2007). Thus the dust plays an important role in space despite of the fact that dust-to-gas mass ratio in the interstellar medium (ISM) is 1% (Bellan 2008), and the knowledge of its sources and constitution is of great importance to astrophysics and astrochemistry.

The information on astrophysical dust can be obtained directly by collecting the dust particles with the space probes (like Titan aerosols) or as a part of meteoritic material (Murchison meteorite). For the distant space objects, such as dust clouds, only source of information are the extinction spectra. The improvement of interpretation of these spectra is thus crucial. In this sense, various laboratory astro analogues were developed that should mimic either a similar dust environment in space or match the extinction spectra of the astrophysical dust (Pendleton and Allamandola 2002). The different dust analogues were proposed for infrared (IR) extinction and the criteria for a "good" carbonaceous astroanalogue established (Pendleton and Allamandola 2002).

The main goal of our work is to answer the question on the possible source of the UV 217.5 nm extinction feature. Physical models of cosmic dust rely on optical properties measured carefully for specific analogue materials available in the laboratory (Sorrell 1990, Colangeli et al. 1995, Zubko et al. 1996). Their relevance is a function of their compatibility with the observational and cosmic abundance constrains. Small graphite spheroid grains ($r \leq 20$ nm) are usually used for modeling optical properties (Sorrell 1990). To satisfy the observational constrains, especially the peak position, the dielectric function of graphite has been modified in most of the models to account for different morphology and clustering state (Colangeli et al. 1995).

Therefore, to complement the theoretical approach using a tailored dielectric function and an ideal morphology it is important to directly measure the extinction properties of small carbonaceous grains produced in the laboratory. In our previous work we designed and tested the ISM dust astro analogue for IR extinction (Kovačević et al. 2005, Stefanović et al. 2005). *In situ* IR absorption/extinction spectra of carbonaceous dust particles generated in plasma polymerization experiment were analyzed according to the criteria for the "good" astroanalogues, established previously by Pendleton and Allamandola (Pendleton and Allamandola 2002). The matching of IR absorption of laboratory dust analogue with the proposed criteria was excellent. Here we used the same plasma dust analogue as a test object for UV extinction.

In the paper we present the experimental set up and how to generate the carbonaceous astro analogue in the laboratory, by using the plasma polymerization of hydrocarbon precursor. The preliminary results on UV extinction and their comparison with the predicted extinction curves are also presented, together with a short discussion and a summary.

2. EXPERIMENT

Our experimental set-up was discussed in detail previously (Kovačević et al. 2005, Kovačević et al. 2003). Therefore we shall give here only a brief description of our experimental set-up and we shall explain a procedure for obtaining carbonaceous nano-particles in laboratory plasma - polymerization experiment.

As a source for plasma polymerization we use standard 13.56 MHz radio-frequency (RF) capacitively-coupled discharge (Fig. 1). The electrode system consists of two parallel-plate stainless-steel electrodes, 30 cm in diameter, and 8 cm apart. Continuous flow of argon/acetylene gas mixture is fed into the discharge chamber at 8/0.5 sccm (standard cubic centimeter) flow ratio. This is our "standard" mixture but it is easy to switch to other background/matrix gas, e.g. helium or nitrogen, or to other monomer gas, like CH_4 or C_2H_4. The input power of 15 W is supplied symmetrically to both electrodes. The gas pressure is set to 0.1 mbar. After various experiments we found these conditions to be suitable for efficient dust polymerization in our experimental set-up. For our discharge conditions, during the dust growth period (approximately 30 min) dust particles levitate in plasma between the electrodes and thus they can be analyzed in situ, avoiding their exposure to the environmental influences. At the end of the growth cycle dust particles reach the maximal size of about 600 nm in diameter and at that time they become too big to be kept in plasma. So they are expelled from active plasma matrix and the new growth cycle starts. As we previously measured the particle growth-rate (about 20 nm/min) we are able to control dust size by switching off the monomer (acetylene) supply at the particular time of the growth cycle: after, for example, 5 min of discharge run the particles reach the size of 100 nm in diameter (or 50 nm in radius).

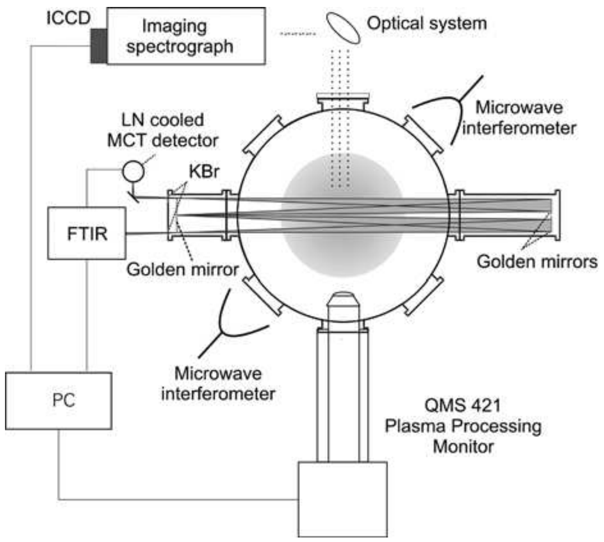

Fig. 1. *Experimental set-up, top view. For the more detailed explanation and abbreviations see text.*

For detection and spectral analysis of nano-particles we use Fourier Transformed Infrared Spectrograph (FTIR) (Bruker), which allowed us to measure IR absorption spectra from 500 cm^{-1} to 7000 cm^{-1} simultaneously. The spectrograph samples an area of 2 by 10 cm^2 through the center of the discharge. We use multi-pass White cell to increase detection limit of our system (7.2 m absorption length). The Plasma Process Monitor (PPM) is mounted perpendicular to the discharge axis and is used to measure the plasma species mass constitution (neutrals and ions) as well as ion fluxes. This gives us a better understanding of the influence of dust particles on the plasma condition. To measure the electron density in the plasma, we used microwave interferometer working at wavelength of 1 cm (Berndt et al. 2006). The plasma emission spectroscopy is performed by using the imaging spectrograph supplied with the Intensified Charged Coupled Device (ICCD) camera. All of the equipment listed is driven by personal computer(s) (PC, in Fig. 1 only one is shown), where all the data are transferred and stored. Measurements of the nano particle UV extinction curve were carried out by means of a UV (180 nm to 300 nm) or VUV (vacuum UV, 120 nm to 240 nm) spectrograph, equipped with a photomultiplier. The Deuterium Spectral Light Source was mounted in front of the CaF_2 windows to extend the spectral range to the 120 nm VUV region. The extinction measurements make the basis of the current article.

3. RESULTS AND DISCUSSION

Recently, we proposed and analyzed a new plasma generated analogue for astrophysical dust (Kovačević et al. 2005, Stefanović et al. 2005). The analogue was obtained with the experimental set-up already described in this paper and tested according to the criteria for the good analogue (Pendleton and Allamandola 2002). The amorphous hydrocarbon dust was found in different directions in our or in neighbouring galaxies (Pendleton and Allamandola 2002). Pendleton and Allamandola (2002) made an extended analysis of candidate materials proposed as relevant to the organic refractory material in the Diffuse Interstellar Media (DISM), concerning the spectral constraints in mid-infrared region between 4000 cm^{-1} and 500 cm^{-1}. The criteria are briefly summarized as: (i) the shape and structure of 2900cm^{-1} aliphatic CH stretch band profile; (ii) ratio of the optical depth of the aliphatic CH stretch feature to the optical depth of the OH stretch peak near 3200 cm^{-1}; (iii) ratio of the optical depth of the aliphatic CH stretch feature to the optical depth of the carbonyl band near 1700 cm^{-1}; and (iv) ratio of the optical depth of the aliphatic CH stretch feature to the aliphatic deformation modes near 1470 cm^{-1}. It came out that plasma polymerized carbonaceous dust match excellently all spectroscopic constrains in mid-IR spectral region.

The second very important spectroscopic indicator of a presence of carbonaceous space component is the UV extinction at 217.5 nm, the so cold "UV bump". This spectral feature, clearly present on the extinction curve, was already a subject of various investigations, including the laboratory analogue extinction measurements (Schnaiter et al. 1998, Colangeli et al. 1995, Zubko et al. 1996). The 217.5 nm feature is believed to come from the absorption in π - π^* transition in graphite or amorphous carbon grains. The importance of its origin is closely related to the question of carbon abundance in the solid phase of ISM (Sandford 1996) and the evolution of amorphous hydrocarbon dust (Sorrell 1990, Colangeli et al. 1995). The main question is: Is the same material the source of UV (217.5 nm) and IR (2900 cm^{-1}) extinction?

We turn to this problem by measuring the UV extinction curve of our proposed dust analogue. Fig. 2 shows extinction curves obtained from particles produced in argon/acetylene plasma. The different curves are obtained for different particle growth-times i.e. different particle radii/diameters, ranging from less then 10 nm (15 s discharge time) up to 50 nm (5 min discharge time). Our previous results show that plasma polymerization process in our experimental conditions produce monodisperse, cauliflower-like particles (Stefanović et al. 2005). During the particle growth they levitate between the electrodes and as they are negatively charged there is no coagulation between them, which makes them an ideal object for testing dust extinction models (Schnaiter et al. 1998). At the early stage of production (first 10 s - 30 s) there is a very rapid growth of the particles and after that time the particles growth is linear, about 20 nm/min. Thus different curves are connected to the different times after starting the discharge or different particle diameters. There are also two sets of curves plotted: one that was taken with UV/visible spectrograph and ICCD camera, and the other that was collected by using the VUV spectrograph, with the wider spectral range, equipped with the photomultiplier. It should be underlined that two sets of curves were measured in independent measurements separated by a long period of time. There is an excellent matching of the absolute values of the absorbance for the particles of the same diameter obtained with the different spectroscopic systems. This is a confirmation of the high reproducibility of the experimental conditions, particle characteristics and measurement technique. An increased dispersion of experimental data around 140 nm is a consequence of declining quantum efficiency of the optical system.

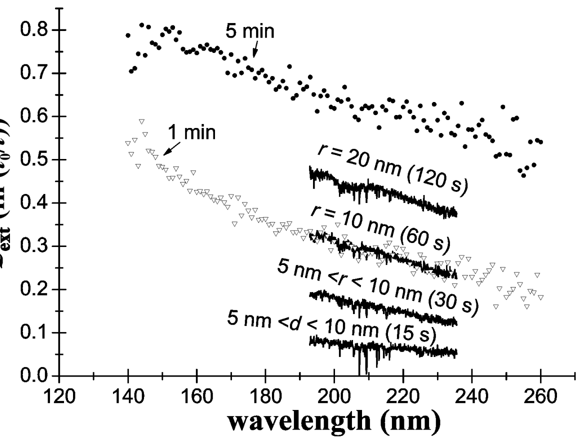

Fig. 2. *Extinction curves (Q_{ext}) for different particle radii (different discharge times). UV extinction curves are measured with two different spectrographs/detecting systems: solid lines - extinction measured with UV/VIS spectrograph and ICCD; solid circles and opened triangles - extinction curves for extended spectral region (VUV).*

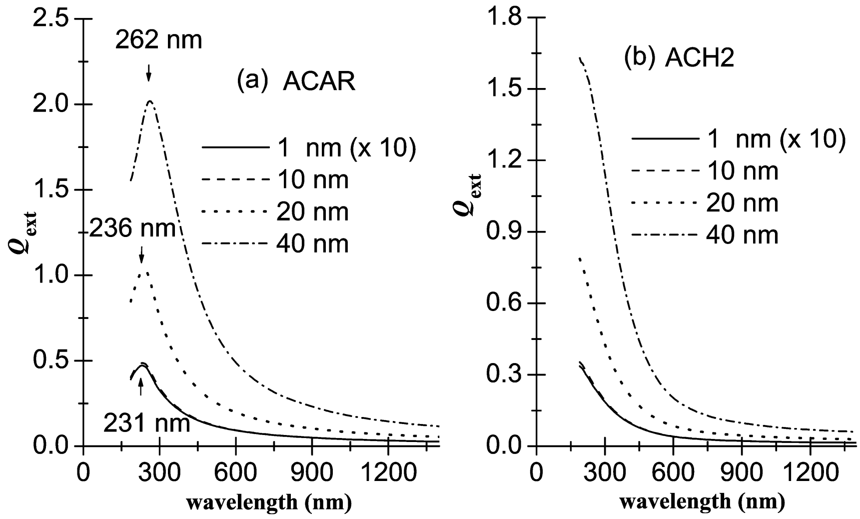

Fig. 3. *Extinction curves for different particle radii. The refraction index necessary for the calculation of Q_{ext} was taken from Zubko et al. (1996): (a) low-hydrogenized material, graphitic-like (ACAR); (b) hydrogen-rich material, polimer-like (ACH2).*

The extinction efficiency Q_{ext} of spherical particles depends on the complex refraction index of the particle, which itself depends on the material properties and on the particle radius. Figs. 3a and 3b show the extinction efficiency for two kinds of carbonaceous materials and for different particle radii calculated according to Bohren and Hufmann (1983). Values of complex refraction index n were taken from Zubko et al. (1996), who determined n over a large wavelength interval for different carbonaceous materials. The material used for the calculation of the extinction curves in Fig. 3a ("ACAR") represents a low-hydrogenised material, which was produced in an arc discharge working with graphite electrodes in argon atmosphere. The results presented in Fig. 3a show that the extinction curves for ACAR exhibit maxima located around 231 nm for small particles ($r \approx 10$ nm). With increasing particle radius, the maximum is shifted towards larger wavelengths. The material used for constructing Fig. 3b ("ACH2") was produced in an arc discharge with graphite electrodes in an atmosphere containing hydrogen and represents largely hydrogenised material. In contrast to the ACAR, the extinction curves in Fig. 3b do not show any maxima. This behavior is consistent with the results of annealing experiments (Mennella et al. 1995), which showed that, with the depletion of hydrogen, energy gap closes and the amorphous material becomes more "graphitic-like".

Finally in Fig. 4 we compare our measured UV extinction with the calculated extinction curves for ACH2 material. Both, experimental and calculated, curves were normalized to the unity at 250 nm. They monotonically increase towards the shorter wavelengths, with no distinct spectral feature. The measured data for different particle sizes show the same trend as the calculated ones: the steepness of the curves decreases towards larger particle sizes. This is in agreement with previous measurements of Colangeli et al. (Colangeli et al. 1995) for ACH2 sample, which has a similar IR signature as our hydrocarbon nanoparticles, but different from the matrix isolated nano-sized carbon grains form (Schnaiter et al. 1998), with the similar IR spectra. According to Schnaiter et al. (Schnaiter et al. 1998), the optical properties of carbonaceous grain material are strongly influenced by the particle shape and the clustering degree. Our particles could be considered as isolated, similar to the situation described by Schnaiter et al., with the difference that our matrix was in gaseous form.

One possible explanation for missing UV bump follows from the results of Sorrell (Sorrell 1990). This author calculated surface plasmon excitation in semi-amorphous solids showing metallic properties, like graphite. He found that the 217.5 nm absorption feature has Lorentzian profile with the damping constant Γ_0 exhibiting minimum for the very narrow interval of particle radii, between 6 to 8 nm. We estimated the minimum particle radius in our experiment to be greater than 10 nm. According to the IR extinction and NEXAFS measurements (Kovačević 2006), our particles are the mixture of sp^3 amorphous material with the islands of sp^2 graphitic - component. With the decrease of the particle size, the contribution of sp^2 may become more dominant. Recently, we found the method for creating nanoparticles with tailored properties, e.g. $sp^2/\ sp^3$ ratio, by using different background/matrix gases (Kovačević 2006). With helium replacing argon we obtained nanoparticles with larger $sp^2/\ sp^3$ ratio. In the

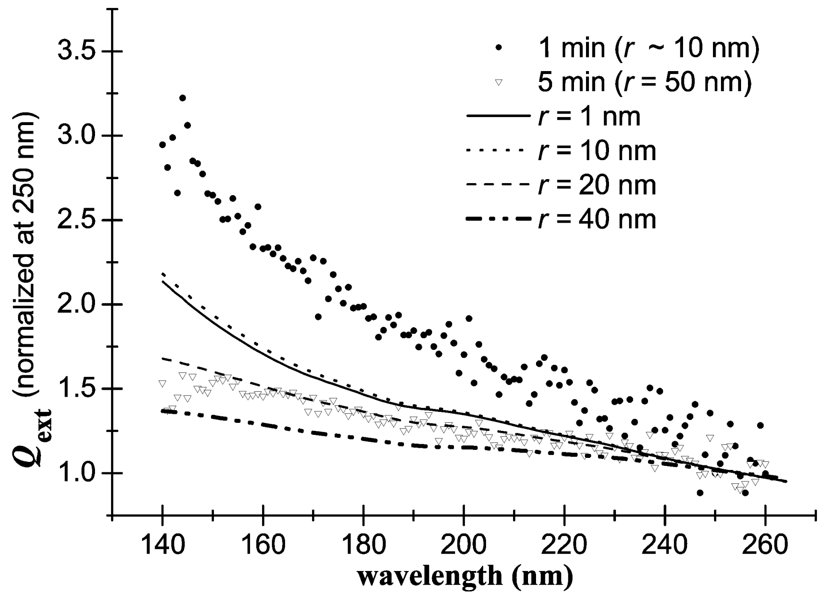

Fig. 4. *Comparison of calculated and measured UV extinction curves for different particle radius: solid lines - calculated curves for ACH2 material according to Bohren and Huffman (1983) with Q_{ext} from Zubko et al. (1996); symbols - measurement results.*

future experiments we shall use this possibility to trace the differences in UV extinction spectra, as it was already detected with IR spectra for particles obtained in C_2H_2/Ar and C_2H_2/He mixture (Stefanović et al. 2005).

4. CONCLUSION

In this paper the UV extinction curves of carbonaceous dust particles with radius between 10 nm and 50 nm are presented. Different measurement techniques applied have shown that the experimental set-up and the procedure for obtaining plasma dust analogue are highly reproducible, even over long period of time between the consecutive measurements, making this technique competitive to the other methods for obtaining laboratory dust analogues (Schnaiter et al. 1998, Sorrell 1990, Colangeli et al. 1995, Zubko et al. 1996). The second important feature of the proposed ISM carbonaceous dust analogue is that the dust particles are spheroid, mutually isolated and there are no clustering effects, which makes them favourable for testing dust extinction models (Schnaiter et al. 1998). Plasma polymerized dust analogue suffers no "matrix" effect because they are weakly coupled to the surrounding plasma environment (concerning their light extinction properties), thus making them different from the already proposed matrix isolated dust analogues, which are embedded in a solid state phase (Schnaiter et al. 1998). The already proposed and characterized plasma polymerized astro-analogue for carbonaceous dust in the ISM (Kovačević et al. 2005) exhibits no resolved spectral feature at 217.5 nm. Comparison of the calculated and measured extinction coefficients shows that the plasma polymerized dust particles in acetylene/argon mixture have rather an amorphous hydrocarbon structure than a graphitic one. In the separate measurements, we analyzed the chemical constitution of our dust particles *ex situ* and found about 40% of hydrogen. This is in agreement with results reported in the literature for ACH2 hydrogen - rich analogue (Collangeli et al. 1995), except that our particles were isolated in gaseous matrix and had no coagulation. The particle size in both experiments was similar but different from another important measurement of the hydrogen- rich dust analog (Schnaiter et al. 1998). Schnaiter et al. reported the dust particle sizes of 5 to 15 nm, that are believed to be the source of 217.5 nm extinction feature. As the source for 217.5 nm absorption is connected to the graphitic (low-hydrogenized) component of dust material the explanation for the presence of this feature in hydrogen-rich material is that with the decreasing of the particle size the sp^2 cluster sites in amorphous environment become more dominant. In the opposite case, with the larger particle sizes (larger than 10 nm) the influence of sp^2 sites diminishes and the 217.5 nm feature disappears.

To get a better insight in the problem of 217.5 nm carrier we shall improve production, control and managing of very small particles, of the order of 6 to 8 nm, which are expected to show increased 217.5 nm extinction. The possibility of creating nanoparticle with tailored properties, especially sp^2/ sp^3 ratio, which seems to be crucial for the UV extinction of nano-sized dust particles, will improve our knowledge on UV extinction spectra of hydrocarbon dust.

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ПРАШИНА ГЕНЕРИСАНА У ПЛАЗМИ КАО АНАЛОГОН ЗА ЕКСТИНКЦИЈУ НА 217.5 nm

I. Stefanović[1,2]

[1] *Institute for Experimental Physics II, Ruhr University Bochum 44781 Bochum, Germany*

[2] *Institute of Physics, University of Belgrade, POB 68, 11080 Belgrade, Serbia*

E–mail: *ilija.stefanovic@rub.de*

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Оригинални научни рад

У овом раду приказани су резултати мерења ултраљубичастог спектра екстинкције карбонских наночестица, у опсегу од 140 nm до 260 nm. Као астроаналогон "мистериозне" међузвездане екстинкције на 217.5 nm коришћен је претходно испитани аналогон који одлично описује екстинкцију у инфрацрвеном делу спектра.