Eur. Phys. J. D **26**, 151–153 (2003)
DOI: 10.1140/epjd/e2003-00280-8

THE EUROPEAN PHYSICAL JOURNAL D

Reply to the comment on

Regenerative soot as a source of broad band VUV light

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Eur. Phys. J. D **22**, 189 (2003)

Received 30 July 2003

Abstract. Certain important and pertinent questions have been raised by E. Träbert in his comment on the paper [1] by one of us. We provide explanations as well as new and recent data using a calibrated monochromator on the existence of the main intercombination multiplet 233 nm which is the bone of contention. It is shown that there is no conflict with the established atomic physics in the regenerative sooting discharges; only the interpretations are at variance with those of the comment.

PACS. 32.70.Fw Absolute and relative intensities – 34.50.Dy Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions – 34.80.Dp Atomic excitation and ionization by electron impact

Our recent communication on the prediction of the regenerative soot being the source of VUV light [1] has been commented upon by E. Träbert. His comment is primarily based on four points; (1) the lack of clear information about the sooting discharge source and the ambiguity in the definition of the regenerative soot, (2) doubts about the authenticity of the spectrographs and the identifications of the lines therein, (3) the difference between the state of excitation of the C ions claimed in our sooting discharges at relatively higher pressures $\sim 10^{-2}$ to few mbar compared with those created in advanced sources like ECR, ionized and maintained in traps and storage devices at UHV $\sim 10^{-9}$ mbar, and finally (4) whether the analysis and interpretations of our data is in conflict with the established atomic physics? These indeed are relevant observations and we will attempt to provide an appropriate reply herein.

The mass spectrometric data from the regenerative soot prompted us to claim that it can be used as a source of carbon clusters C_m ($m \geq 2$) in a number of articles [2]. Later on, the analysis of the emission spectroscopy of these discharges in the UV and visible range provided us clues to the state of excitation and ionization of monatomic C (C I, C II, C II, ...). The possibility of using sooting discharges as light source with special properties depends on whether the indirect evidence in the form of intense intercombination lines of C II and C III can be interpreted as a proof of the existence of highly excited states of the singly and doubly charged C ions; we will discuss this later in this reply. References [2,3] described in detail the development of the concept of the "regenerative soot" along with the experimental methods and the techniques of producing soot and its regeneration. It is the regenerative process that ensures a graphite hollow cathode's use either as a source of carbon clusters C_m ($m \geq 2$) or a light source. It critically depend on (a) the accumulation of clusters within the discharge and on the graphite hollow cathode surface, (b) the support gas and its pressure, (c) the external magnetic field whose 3D contours within the hollow cathode trap electrons and ions and (d) the discharge current i_{dis}. A sooting discharge in graphite hollow cathode is initiated by the kinetic sputtering of the sp^2 bonded carbon atoms by the energetic ions of the discharge support gas. These C atoms could be in mono-, di-, tri- atomic or even higher molecular combinations. Once released from the substrate graphite, these free radicals participate in all energetic activities of the discharge. This C cluster containing glow discharge provided us with the evidence for the existence of all sorts of C clusters in the mass spectra [2]. Whereas, the mass spectra clearly identifies the existence of the C clusters C_m, the emission spectra on the other hand, shows the transitions from the excited and ionized monatomic C. If one monitors the sequences of the C liberation from the graphite surface to C as participant in the discharge through the successive emission spectrographs,

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then a picture of the state of excitation and ionization of the carbonaceous discharge emerges. The special features of this "soot-in-the-discharge" as defined by Träbert or our "regenerative sooting discharge" is that it contains those excited states that result in the population of the ^{4}P metastable state in the case of C II. That was our assertion in reference [1]. Some more data on the existence of quartet-quartet and doublet-doublet transitions of C II has recently been published elsewhere [4].

Regarding the issues of the authenticity of the spectral line identification, wavelength calibration and other essential requirements of a trustworthy spectrum as pointed out by Träbert, we would like to make a basic points that for our carbonaceous discharge the emission spectrum itself provides the calibrating peaks in the entire wavelength range from 185 to 600 nm. For example, in the initial stages, the C I lines at 193 and 248 nm provide the first signatures of C's inclusion as a sputtered species in the discharge as well as the data markers. Various lasers were used for wavelength calibration of the monochromators. The usual lines of He, Ne, Xe and other support gases are always there and provide additional checks. The gradual appearance of C III's 230 nm and C II's IC multiplet at 233 nm are a feature of the discharge that contains soot or the C clusters as identified by the simultaneous mass spectrometry. These features makes the line identification task easier in the regenerative sooting discharges. We have used different monochromators from Jobin Yvon and Jarrell Ash for obtaining the earlier emission data however, for the purpose of providing undisputable evidence for the existence of at least C II's IC 233 nm multiplet, a recent spectrum from a mildly sooting discharge is presented in Figure 1. The spectrum is taken by McPherson monochromator model 2035, a 0.35 m Czerney-Turner device whose wavelength calibration is done through their own Hg lamp. The 5 decimal point accuracy of the lines is a feature of the software provided by the manufacturer. However, due to the larger slit width and the need to optimize the data acquisition time, a lower resolution FWHM ~ 2 Å with stepper motor steps of 0.5 Å is used. The source is operated with He as the discharge gas and has He I's singlet-singlet and triplet-triplet transitions in the higher wavelength regime as discussed in [4]. We have chosen to show the most contentious features of such a spectrum *i.e.* the C III 230 nm line and C II's 233 nm IC multiplet. The inset shows the enlarged version of the 233 nm multiplet. The multiplet peak at 232.55321 Å with a subsidiary peak at 238.00 Å. Does this indicate the preponderance of $^4\mathrm{P}_{3/2}$'s spin forbidden transitions to $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$, respectively? A better resolution will certainly provide much more convincing arguments; such an experiment is in the planning stages. We are planning experiments for the simultaneous absorption and emission by the sooting discharge using the synchrotron radiations in the VUV range. At present the source is being tested with commercial UV light sources. Any collaborations are welcome.

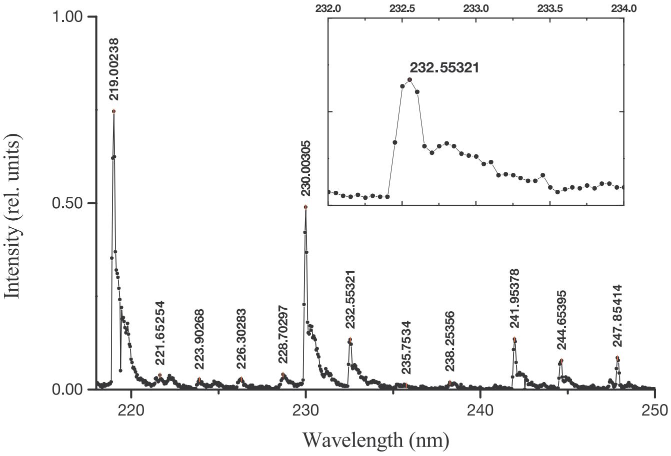

Fig. 1. The figure shows a selected portion of the spectrum obtained by McPherson 2035 monochromator from a sooting discharge in graphite hollow cathode source that was shown in Figure 1 of Eur. Phys. J. D **22**, 189 (2003). The wavelength labeling is done through the manufacturer's software with 0.5 Å steps of the stepper motor. The accuracy of the steps can be visually checked in the inset that contains 40 data points in a 20 Å range. The inset shows the enlarged view of the C II 233 nm IC multiplet. A 2 Å wide peak at 232.55321 nm is the higher intensity line within the multiplet with a less sharp one at 238.00 nm.

Why do the C^+ and C^{++} ions behave differently in Träbert's UHV system and our high pressure sooting discharges is the moot point of the summit which prompted the commentator to shed his doubts on our findings. Primarily the difference lies in the mode of production as a single species in his and other C ion production techniques mentioned in the latter half of the references cited in the comment and the technique adopted by us. They generally create C ions in ECR or some other C molecule (CO, CH_4) dissociating source followed by the excitation and ionization with electron beams and retention in traps or the storage rings for evaluating the spin-forbidden decay times of the metastable levels. Their excitations are from the ground states upwards and follow the usual routes of successive higher levels excitation as a function of the electron energy and the corresponding collisional strengths. We, on the other hand, produce C and its ions by the dissociation of the C cluster C_m, where m varies depending on the state of sooting. The agents of dissociation are the electrons and the support gas metastable atoms. The uniqueness of the regenerative sooting discharge lies in the simultaneous formation and fragmentation of its C clusters within the same source that may follow a route $\sum \mathrm{C}_x$ $(x = 1, 2, ...) \rightarrow \mathrm{C}_m$ $(m \geq 2) \rightarrow k\mathrm{C}_1 + n\mathrm{C}_2 + ...$, where C_m may be excited or ionized. This chemical equation may or may not be reversible depending upon the sooting stages of the discharge. The end products (C_1, C_2 ...) are generally in higher states of excitation and ionization according to our observations. The energy pumped into the discharge is recycled through the processes of the formation and fragmentation of C_m. Therefore, the collisional partners *i.e.* the electrons, clusters, metastable atoms and ions retain energy in the excited and ionized species in these sooting discharges. This, in our view, is the difference between the collisional de-excitation of ions in storage rings at UHV and a completely different pattern observed in the high pressure sooting discharges.

The regenerative soot as a source of C clusters or a source of light is only going to add just another technique for the study of soot with the maneuverability of its reactivation or the recycling between its various species. Träbert's comment that why have spectroscopists not seen it before; the answer is that perhaps they did not use graphite hollow cathodes to create C vapour and to play with the C clusters in the formative and fragmentative stages. It may also be pertinent to point out that there is almost one and a half century between the synthesis of benzene and Buckminster fullerenes; historically speaking, there was at least one misreading the mass spectra [7] so close to C_{60}'s discovery! The two widely different techniques for the production of C_{60} by Kroto *et al.* [5] and Kratschmer *et al.* [6] is the case in point. While Kroto and Smalley used multi-million dollar lasers and UHV equipment with time-of-flight diagnostics to discover C_{60} but only in very small quantities ($\ll$ nanograms); Kratschmer and Huffman used glass bell jars and high pressure arc discharge with cheaper chemical techniques for the separation and gram scale production of C_{60}. A relevant message in these two totally different techniques to produce the same material is that simpler methods may achieve what more complicated ones may not be geared for.

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