OPTICAL RADIATION FROM FULLERENES IN THE GAS PHASE

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Introduction

In spite of large number of works on the physics and chemistry of fullerenes there are still virtually no date on the radiative properties of fullerenes in the gas phase. In the present report we discuss our results of a study of the effect of C_{60} fullerene vapors on the emission spectra of inert-gas discharge plasma and the possibility of using C_{60} as an emitting additive of a gas discharge light source.

Several factors, concerning physical and chemical properties of fullerene molecules [1], lead to the hypothesis that fullerene can be a suitable additive for a low pressure gas discharge light source.

They are as follows:

1) a low ionization potential 7.6 eV;
2) theoretically predicted optical transitions between excited levels in a range 200-260 nm (Figure1).
3) molecules C_{60} do not dissociate during the collisions with fast electrons (up to energy 80-100 eV) or absorb UV photons (with energy up to 30 eV);
4) fullerene is stable to heating up to 900-950°C;
5) the pressure 10^{-2}-10^{-1} Torr of fullerene vapour is reached at 600-700°C;
6) fullerene molecules have practically no ecological effects;
7) it is not aggressive to other materials.

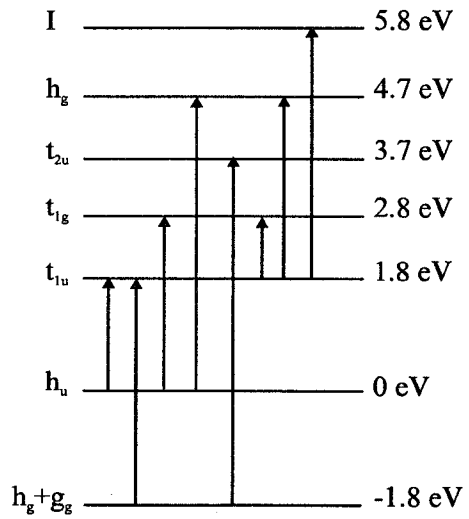

Figure 1. Diagram of the electronic terms of the C_{60} molecule [2]

Experimental

The possibility of using fullerene molecules as the emitting additive in a gas discharge light source was verified on electric discharges in noble gases He, Ne, Ar and Xe. Fullerenes were introduced into the discharge chamber in the form of both C_{60} powder and a fullerene-containing soot obtained by the Krätschmer-Huffman method. Soot in which the fullerene content was reduced to less than 0.01% by means of additional purification was introduced in the control experiments. The discharge chambers were made from transparent quartz glass allowing measurement in a spectral range 200-800 nm with the wall heating up to 700°C. Two types of discharge were studied: d.c. discharge and h.f. inductive discharge at 60 MHz. The noble gas pressure varied within 1-30 Torr and the discharge current density was about 10^{-2} A/cm^2; the h.f. discharge power was high enough for the optical emission to be observed by with the naked eye.

The plasma emission spectrum was measured in the range 200-800 nm at various temperatures of the discharge chamber, various gas pressures and discharge current.

It was observed that when the discharge chamber is heated in the presence of a fullerene-containing material the emmision spectra of the plasma changes in the cases of both d.c. and h.f. discharge. When the temperature of the chamber walls is of the order of 300K, the presence of a fullerene - containing material in the discharge chamber had virtually no effect on the properties of the discharge in inert gases and the emissin spectrum of the plasma in this situation consisted of separate spectral lines which are characteristic for inert-gas atoms on a background of a weak continuous spectrum consisting of the bremsstrahlung of electrons colliding with inert-gas atoms and ions.

As the temperature of the walls of the discharge chamber was increased a radical change occured in the spectrum: the intensity of the spectral lines of the inert-gas atoms dropped strongly and new emmision lines and bands appeared in the blue-green and ultraviolet regions of the spectrum (Figure 2).

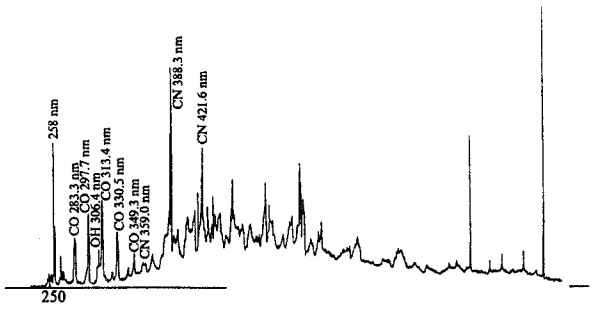

Figure 2. Emission spectrum of an hf discharge in argon.

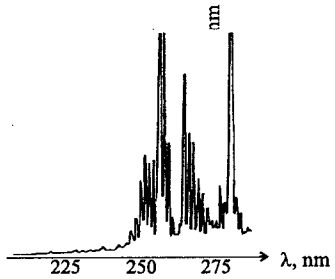

Figure 3. Emission spectrum (near 260 nm) of an hf discharge in argon in the presence of C60 vapor in the gas phase.

Results and Discussion

The spectrum which we observed in much richer than optical emission spectrum of an arc discharge in the process of formation of fullerenes by the Krätschmer-Huffman method [3,4], where Swan bands in the region 437.5 - 563 nm and strong atomic-oxigen band at 247.9 nm were observed.With the exception of a band of lines near 260 nm, which is shown in greater detail in Figure 3, the bands and lines that appear can be identified with C_2, CO, CN, OH and H bands and lines observed previously in the spectra of gas-discharge plasmas.

We attribute the band near 260 nm to the presence of the C_{60} fullerene in the gas phase. This conclusion is drawn on the basis of the fact that this band appears only when a fullerene-containing substance is added to the gas phase and, conversely, it does not occur when the same soot but with the fullerenes remuved is added. Appearently, under the gas-discharge conditions found, energetic excitation of C_{60} molecules occures accompanied by transition of electrons from occupied states HOMO and HOMO-1 into unoccupied states LUMO and LUMO-1 [5]. As concentration C60 molecules in the gas phase increases, which is achived by increasing the temperatures of the walls of the discharge chamber, the new channel - ($C_{60} \Rightarrow C^*_{60}$) for transferring the energy of the gas discharge becomes more efficient than the standard channel via the excitation of inert-gas atoms. Then, this excitation, a unigue excitation, decays with the emission of a photon: $C_{60}^* \Rightarrow C_{60} + h\nu$. It makes sense to assume that the one-electron terms of the excited fullerene C_{60}^* are identical to the terms of unexcited C_{60}. Then data on the optical absorption process $C_{60} + h\nu \Rightarrow C_{60}^*$ can be used to identify the observed line. For example in [6], where the absorption spectra of C_{60} vapor in the temperature range 500-700 C were studied, three strong peaks were observed at 205, 257, and 330 nm. These energies are close to the theoretically computed values (Figure 1) and therefore the 258 nm ($h\nu$ = 4.8 eV) emission line which we observed can be tentatively attributed to the transition $h_g \Rightarrow h_u$, which is symmetry-allowed in the dipole approximation.

We call attention to the well-resolved fine structure of the emission band of a gas discharge in the presence of fullerene vapor (see Figure 3). We assume that this structure is associated with the electronic-vibrational states of fullerene. First, the scale of the fine structure is close to the possible energies of the intramolecular vibration of C_{60} fullerene and not lighter fragments of the type C_3 and C_4. Moreover, the energy position of the main emission line of these fragments is different Second, the ratio of the intensities of the lines and bands, which is similar to that observed in molecular-gas plasma, changes as the temperature increases.

Conclusion

In summary, optical radiation of C_{60} fullerenes in the gas phase was observed. It possible to draw a conclusion that under some discharge conditions fullerene molecules, being added to a buffer gas (as mercury, being added to argon in luminescent lamps), can form emission properties, ionization balance in the plasma of a discharge and absorb the major part of applied electric power. Similar picture takes place in mercury luminescent lamps and ensures their high efficacy.

Acknowledgments

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References

[1] S.V.Kozyrev, V.V.Rotkin. Sov.Phys. Semicond, 1993, v.27, p.777.

[2] V.I.Srdanov, C.H.Lee, and N.S.Saricifici. Thin Sol.Films. 1995, v.257, p.233.

[3] Y.Saito, M.Inagaki. Jap.J.Appl.Phys., 1993, v. 32,p.L954

[4]. D.Afanas'ev , I.Blinov, A.A.Bagdanov et al. Sov. J.Tecn.Phys. 1994, v.39, p.1017.

[5] S.Samuel. Int.J.Mod.Phys., 1993, v.7, p.3877.

[6] S.Dai, L.Mac Toth, G.D.Del Cul et al. J.Chem.Phys. 1994, v.101, p.4470