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THE ARC DISCHARGE WITH A DIRECTIONAL GAS FLOW: SYNTHESIS AND PROPERTIES OF FULLERENES

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ABSTRACT *:In the discharge with a hollow electrode with the gas flow direction of formation and duration of the trajectory forming in the space with a high plasma density and temperature longer so in the sediment synthesis product is not marked amorphous carbon, but the increased output of heavy fullerenes. The calculations of the fundamental characteristics of heavy fullerenes. It noted the dependence of the spectrum and the uncertainty of the parameter stability of the fullerene ion depending on the sign of the charge of fullerenes, and the preferred use of ions fullerenes.*

KEYWORDS - Amorphous component, electron affinity, formation duration, gas-plasma stream, hollow electrode, hydrogenated cluster, stability of fullerene ion, turbulence.

INTRODUCTION

General provisions

In the 1970s, the possibility of the existence of hollow C_{20}, C_{60} clusters and their electronic structures were shown theoretically [1]. These carbon clusters were called fullerenes. Фуллерен C_{60} имеет диаметр 0.714 nm. These structures were obtained experimentally in a supersonic helium stream by the action of a laser beam on the graphite surface [2]. Investigations showed that fullerenes are effective electron acceptors and form compounds with new properties with atoms of other elements. The discovered peculiarities show fullerenes and their derivatives to be a new class of molecules-compounds; the trends in physics, chemistry, biology, medicine and technology, which are originating on their basis, are also new.

Big hopes are tied with water-soluble form of fullerenes, which allow you to enter the sphere of the use of different salt solutions including the lymph and blood person, and directly related to determining the health of the person. In ongoing studies [3], to develop methods to obtain more stable form of output. Therefore it was intended to carry out a technological revolution by modernizing the main spheres of activity through the use of fullerenes, their derivatives and composites based on them as the main material. The advantage and the need for such materials and their production technologies (nanotechnology) is that they provide an opportunity to resist the unrestrained population growth consumption of energy and materials using processes harmless to humans and the environment.

To realize this idea, a search for and development of fullerene synthesis methods were initiated. At the present time, the most commonly used fullerene synthesis methods are: laser [2], chemical [4] and arc discharge [5] methods. The common peculiarity of the methods is that fullerene synthesis takes place in an inert gaseous medium at the temperature $1500 < T < 7000$ K [6] (low - temperature plasma conditions). The formation of nanostructures in a space with high temperature takes place by collision of carbon clusters. The process is affected by the Coulomb interaction of particles with opposite sign. The synthesis methods differ in fullerene formation mechanism, but the results of the last few decades

have shown that methods within the measurement error have a limit value output $\eta = (19 \pm 4)$.

New methods for the synthesis of fullerenes have relatively smaller history, experimental basis, and have defects. For laser method disadvantages are: low percentage conversion of pump energy into the energy of the beam, the opacity of carbon vapor laser beam and the problem of radiation entering the cell fusion. For the chemical method is characterized by a low percentage of conversion of carbon clusters in view of the complete structure of the fullerene conversion features polycyclic aromatic hydrocarbons (PAHs) [7] at a low value of optimal synthesis temperature ($T \leq 2000$ K). Further development of laser and chemical methods probably will eliminate the deficiencies noted. But arc plasma medium on the basis of carbon vapor is an indispensable element to maintain the continuity of the arc and the synthesis process. Discharge control elements are: the geometry of the electrode discharge, gas atmosphere and arc discharge parameters. An additional advantage of the method is the experience of creating and using a wide range of bit devices and the equipment for arc discharge.

The aim of this work is a more detailed discussion of the features of the new method of arc synthesis of fullerenes, which showed a significant advantage in comparison with the approved methods, and to study insufficiently known the fundamental characteristics of heavy fullerenes.The content of this article at the urging wseas.org the proposal is in addition to the advanced [8], therefore presented in the materials obtained primarily from the same experimental facilities, but some parts are abridged. Therefore, to complete its consideration of this issue should be handeled by [8].

Fullerene Formation Process in Arc Discharge

Fullerene arc synthesis is a multievent process, the theory of which has not been carried to completion. According to general concepts, the C_j fullerene formation process takes place in the discharge space at 1500 – 5000 K during diffusion as a result of collisions followed by coalescence of nanoparticles. Fullerene synthesis is conventionally represented as series of acts of attachment of small C_k, C_i clusters of carbon vapor from the heated portions of the electrodes and the subsequent kinetic excess energy relaxation of coalescing particles in inverse processes, annealing-away of $n_f \cdot C_f$ clusters. Conventional synthesis scheme:

$$C_j = C_к + \sum|_i n_i \cdot C_i - \sum|_f n_f \cdot C_f, \qquad (1)$$

where C_k is the initial fullerene cluster formed in the interelectrode space, the coefficients n_i, n_f are integers. The clusters in the scheme (2) are summed with respect to the subscripts i and f. According to the scheme (2), the formation parameters of each C_j fullerene also develop on the conventional path. The fullerene formation parameters are formed from the sum of individual segments: duration of the formation process, $T_j = \sum|_j t_{Cj}$, and formation path length $H_j = \sum|_j h_{Cj}$.

During the formation stability of the structure is controlled by the annealing process, which is under the influence of atomic bonds at conventional scheme (1) correspond to particles $\sum|_f n_f \cdot C_f$. Structure formed with a number of carbon atoms believe resonance (C_{60}, C_{70},…), because the mechanism of formation of these structures is unknown. In arc discharge, the diffusion nature of spatial motion with temperature decrease from radius gives a spread of clusters in path parameters, in mass and quality of the product. In arc discharge, amorphous carbon black accounts for a larger fraction of the product (> 50%).From the analysis of the existing concepts it may be assumed that the product of other quality can be obtained in a space with high temperature, in which longer duration and length of fullerene formation path with turbulent portions are ensured. The space with such peculiarities has a circular

symmetry at the minimal energy consumption. Based on these ideas, the optimum design is preferred to look at the small gaps between electrodes.

PROBLEM SOLUTION

Arc Discharge in a Hollow in Electrode with Working Gas Flow (ADHE-WGF)

To ensure continuous synthesis process, a stock-produced TDM-317 as welding power source with dropping current-voltage characteristic and a pulsed arcing stabilizer (PAS) were used jointly. The TDM-317 + PAS circuit continuously holds plasma in the interelectrode space, also at the moments of passage of current and voltage through zero [9]. Presented futher design of the discharge device was created based on the original dorobotki devices [10, 11], which was develop a design discharge chamber on the adility to combine the advantages of the marked bit devices. In the works [12, 13], fullerene synthesis was carried out in a chamber of 68 mm diameter (h = 150 mm) on the discharge device shown in Fig. 1: graphite electrode 1 for emission spectrum analysis (diameter 6 mm), graphite electrode 2 (cavity diameter 15 mm, h = 15 mm) with slits through which working gas (He) enters the electrode cavity. The cuts (slots) in transverse and longitudinal dimensions provide education directed jet passing gas. In the design, the part 3 is a graphite cover. Electrical insulation between the electrodes 1 and 2 is provided by a high-temperature ceramic, an alundum crucible 4. An extra function of crucible is heating the working gas that enters the discharge space. The working gas coming from the free space heats on the passage of gas-pasma flow and discharge radiation over the surface of the crucible, which heats up on thermal contact with the heated electrode portion. The parts 5 and 6 of common steel apply potential to the electrode 2 and fasten the construction together into a whole. The part 7 is the chamber wall. In the future, an attempt was made to optimize the design of the camera. It was made graphite electrode – part 2 (on Fig.1) with a cavity diameter of 20 mm, but the trial inclusion product was obtained with a high content of amorphous carbon black.

Product of Synthesis by Arc Discharge in a ADHE-WGF

The composition of the product of synthesis by ADHE-WGF (fullerite) was determined on an AutoFlex apparatus (Bruker, Germany) from a time-of-flight mass spectrum (MS), Fig. 2. This is a MS of fullerenes with negative charge for a product obtained in ADHE-WGF under optimal conditions. As can be seen, the lines in this series follow at the interval Δ (m/z) = 24 amu = $2m_c$, which is usual for fullerene spectrum. It is seen from Fig. 2 that the MS consists of background bands, which differ in height and width, bands of medium hydrogenated clusters (C_{26}, C_{27}, C_{28}), C_{60}, C_{70}, C_{72} and a series of C_{74+2n} lines, where n = 0-40. In the spectrum, the lines of stable nanostructures, which accumulated during discharge on the cooled walls of the chamber: C_{60}^-, C_{70}^-,…, C_{78}^-, C_{84}^-,.., C_{90}^-, C_{96}^-, C_{112}^-,…, C_{150}^- stand out in the value of the peaks. The peak values in the MS of fullerenes in Fig 2 are in agreement with the formation mechanism of scheme (1) and another detailed presentation proposed: the peak values of fullerenes decrease with increasing mass, but the decrease in peak values in ADHE-WGF is smaller as compared with ordinary-arc discharge spectrum. An important peculiarity of the spectrum of ADHE -WGF, which contradicts the above one, is that the peak value of C_{84} fullerene exceeds that of the C_{70} fullerene. The spectrum of fullerenes with positive charge ends with the C_{84}^+ fullerene peak (see below), but the background spectrum has an extension at m/z > 1800 u.

Mechanism of Fullerene Formation in ADHE-WGF

As was pointed out above (1), fullerenes begin to form on collisions of carbon atoms, ions and small C_2, …, C_4 clusters by the action of a turbulent evaporation flow from the surface of the electrodes. But in a hollow electrode, the turbulence under the action of working gas flow is higher, and the process

occurs with the participation of helium atoms via forward and back reactions [14]. Another distinction of the MS of ADHE-WGF from ordinary-discharge MS is background. The structures that create a background in the MS of ADHE-WGF don't affect the transparency of the benzene solution of fullerene carbon black. The background is created by nanostructures formed as a result of "re-formation" of fullerenes and annealing away of fragments, which become just a "nanobackground". The nanobackground peaks in the mass spectrum $24 \leq m/z < 2000$ u have a value of up to 2.0 – 3.5 % of the peak value of C_{60}. The MS of the product of ADHE-WGF at the discharge current I = 70 A without filtration coincides with the spectrum obtained after double filtration. The result is confirmed by the MS of fullerene carbon black synthesized at I = 80 A. There is a background in the spectrum of positive and negative ions, and the background is larger for the product obtained at higher discharge current.

Geometrical Factor in Fullerene Formation Shows the Nature of the Limit Value Outputs

In arc discharge, the length of fullerene formation path is estimated from the equation:

$$L_0 = (1 \div 3) \times \Delta, \qquad (2)$$

where Δ is working interelectrode gap $\Delta = 1 – 7$ mm [15], and the length of fullerene formation path $L_0 \approx 15$ mm.

An examination of the formation space in the device for ADHE-WGF is given on the basis of the size of the electrodes and gas plasma thermodynamics, gives the path:

$$L_1^* \geq 100 \text{ mm}. \qquad (3)$$

In this case the trajectory of the fullerene formation shaped like a helix, which has 2-3 turns. Comparison of the values in (2) and (3) shows an advantage of the method with hollow electrode over that with ordinary discharge: *the fullerene yield is higher at the longer length of nonlaminar formation path.*

THE MEAGUREMENT RESULTS AND DISCUSSION

The synthesized in ADHE-WGF product was analyzed in a solid fullerite phase on an AUTOFLEX ^{R}IILRF 20 time-of-flight mass spectrometer with pulsed N_2 laser (Germany). The mass spectrum negatively charged fullerenes presented in Fig 2. The spectrum was obtained at the discharge current I = 70 A. The values of the peaks of the fullerenes C_{60}, C_{70}, C_{84}, …, C_{150} in the mass spectrum are as follows: 100, 57, 78, …, 6. The descent of the envelope curve of the peaks of fullerene mass spectrum with increasing number of atoms in the cluster is common. This is in accordance with the generalized scheme (1). In discharge with hollow electrode, however, the decrease in the values of peaks is smaller, and the value peak C_{84} is larger than peak C_{70}. The peculiarity apparently shows that the structure of the C_{84} cluster is formed by the optimal number of covalent electron bonds, which have a three-dimensional structure. As a result, the C_{84}^- cluster has been obtained, which is stronger than other fullerenes Fig 2. In mass spectrum is distinguished peaks lines (conditional resonant structures) poorly known fullerene C_{112}, C_{122}, C_{146}, C_{150}. To determine the values of the electron affinity (EA_n) and energy of ionization (EI_n) of fullerenes were made calculations. The calculations are based on a rigid model for the structure of the carbon spheres formed from n carbon atoms with an effective radius of the $R_n = n^{0,5}$. The calculations used in a ratio of adjusted:

$$IE_n = \varphi_\infty - K_1/R_n \qquad (4)$$

$$\text{and } EA_n = \varphi_\infty + K_2/R_n, \qquad (5)$$

where n – number of carbon atoms, K_1 and K_2 – normalization coefficients, φ_∞= 5.37 eV – the work function of graphite sheet. Data for C_{60} were used in the calculations [15]. The results of calculations for noted of heavy fullerenes Fig. 2 are given in the Table.

According Table seen that the ionization energy of clusters decreases with increasing number of carbon atoms, but with the number of carbon atoms increases the electron affinity. Therefore, according to Table between electro-physical parameters of fullerene C_n there is a general relationship:

$$EA_n + IE_n \leq 2\varphi_\infty \qquad (6)$$

The values included in the relation (6) is by definition have a different nature, and show that the mass spectra of fullerene differing in sign of charge fullerenes.

The mass of negatively charged fullerenes spectra Fig 2 obtained at the optimum value of the discharge current is gradually decreases with increasing number of carbon atoms tail, which includes the structure and containing up to 150 and more carbon atoms. In this part of negatively charged ions fullerenes in intensity in 2 to 4 times higher than the background, but for ordinary fullerenes (C_{60}, C_{70}….) the excess over the background of the peak of the fullerene has a value of 50-60.

MSs recorded from fullerite value obtained when the discharge current I = 80 A, is listed on Fig.3. The upper part shows the spectrum of fullerene with a negative charge and a positive charge on the lower half. As seen, they have a lower intensity than in Fig. 2 and run these features: intensity peak C_{84}^- greater, than the intensity C_{70}^-, and in the spectrum of visible line C_{150}^-.

But the picture of the spectrum of positively charged fullerenes has a different character. The spectrum of positively charged carbon structures has much greater background than the background in the spectrum of negatively charged structures. The range starts with small clusters based on the C_2 and C_3(see below). Then, follow the peaks in the spectrum of C_{60}^+, C_{70}^+, C_{78}^+ and fullerene C_{84}^+ near the end, and the rest of the spectrum of the fullerene ions are indistinguishable from background structures. This feature is a sign of the instability of positively charged fullerenes.According to the Table unlike the internal energy of the positively and negatively charged fullerene ratio (6) have more than 10 eV, and electron affinity (EA_i) have larger fullerenes with a large number carbon atoms.

Therefore, the presence of excess electrons from the fullerene is a stabilizing factor structure of fullerene**.** So, the mass spectrum of Fig. 2 registered fullerenes C_{150}^-.

But the spectrum of positively charged ends near the C_{84}^+, and recorded further structures are indistinguishable from amorphous background.Comparison of the spectra shows that the mass spectrum of fullerene negatively charged illustrating more details of the composition of analyte fullerite.A possible reason for this may be greater stability of the electronic structure of fullerene ions with a negative charge. Therefore fullerene with a negative charge is preferably used in the processes of electrodynamics.

In accordance with the provisions of [15] in the calculations of the relations (4) – (6) are determined only by the energy of affinity EA_n and the ionization energy IE_n, but there is no parameter stability of the structure, depending on the sign of the charge of the ion fuller. To the need for this parameter there are data in fig.2 and fig.3. Table marked with *estimates fullerene ions with a positive charge, the receipt of which is not reliable. In spectrum view fig. 3 there are significant value the structures of $C_2H_{1\text{-}3}^+$, $C_3H_{1\text{-}4}^+$. But is known that C_3 structure is not stable [16].

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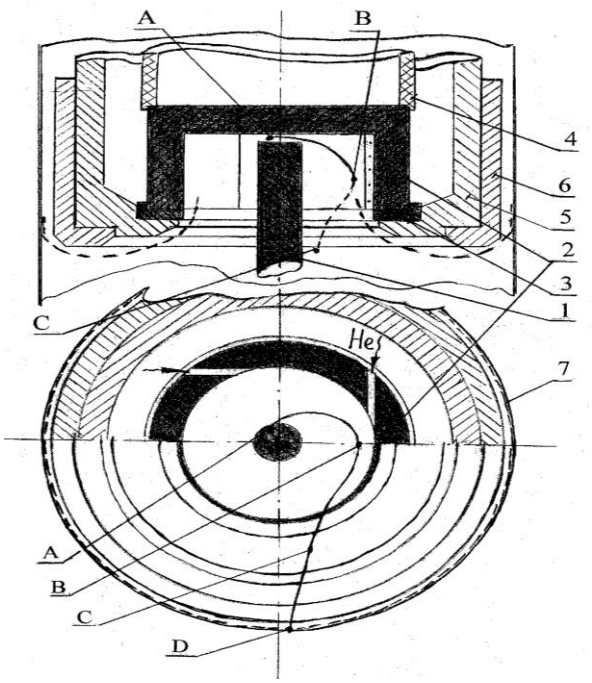

Fig.1. Projections of the parts of an arc discharge device with a hollow electrode and the conventional path A→B→C→D of fullerene formation [8, 17].

Table

The data of fullerenes [15], estimated value of electron affinity (EA_n) and the ionization energy (IE_n) of heavy fullerenes Fig. 2 [17].

Fullerene C_n	EA_n, eV	IE_n, eV	$EA_n + IE_n$, eV	EA_n, eV [15]	IE_n, eV [15]
C_{20}	0,693	10,04	10,733	-	-
C_{60}	2,67	7,57	10,24	2,667	7,57
C_{70}	2,87	7,41	10,28	2,75	7,38
C_{84}	3,09	7,23	10,32	3,15	7,16
C_{106}	3,33	7,06*	10,39	3,41	6,92
C_{112}	3,39	6,98*	10,37	-	-
C_{122}	3,47	6,91*	10,38	-	-
C_{146}	3,64	6,78*	10,42	-	-
C_{150}	3,66	6,76*	10,42	-	-

Fig. 2. Mass fullerene arc hollow electrode, the discharge current I= 70 A, voltage V ≈ 20 V, the parameters of the laser beam:
$q = 2.6x10^{-6}J, f = 0.1s^{-1}$; insertion: a- negative, b-positive[8, 17].

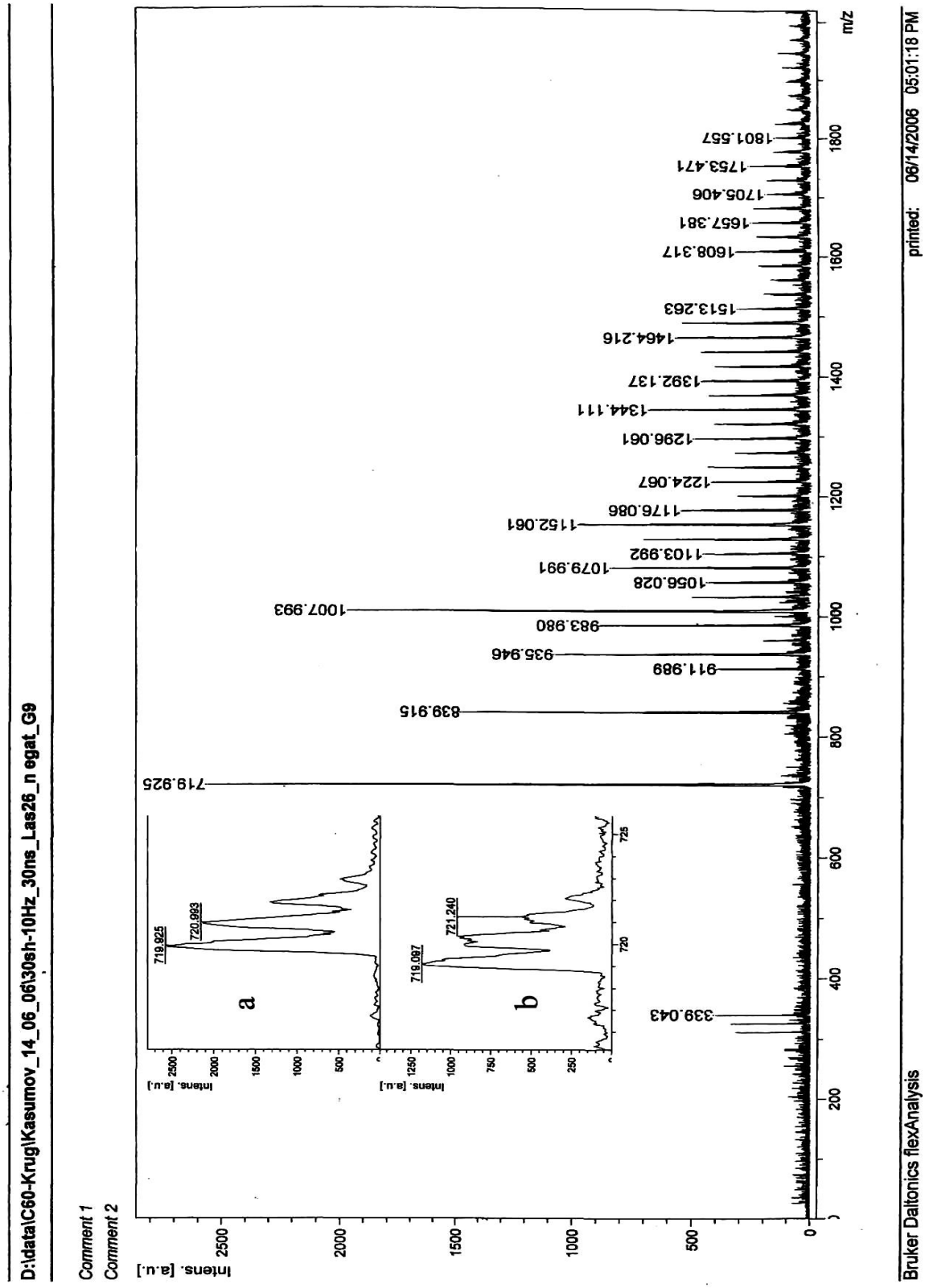

Fig. 3. Mass spectrum of the product obtained in ADHE-WGF with I = 80A after a double filtering; the parameters of the laser beam: $q = 2.6 \times 10^{-6}$J, $f = 0.1s^{-1}$[8, 17].