Coulomb Dissociation of Nanoparticles Grazing along Organic Surfaces

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A Coulomb dissociation model is presented for molecular nanoparticles, e.g. nanoclusters consisting of identical atoms or small molecules. These nanoparticles graze with velocities less than the Bohr velocity (10^8 cm/s) along an organic surface at atomic distances. The surface molecules contain IR-antennas, which consist of periodically located identical diatomic valence bonds with significant dipole momenta, e.g. hydrocarbon chains like $(CH_2)_n$. Here, we analyse the Coulomb interaction of these surface molecules with grazing nanoparticles, which do not contain any IR-antennas, e.g. fullerene molecules. Provided that the grazing velocity is in the range of $10^5 – 10^7$ cm/s and the minimum distance of the grazing nanoparticles to the surface is approximately 2 Å, the IR-antennas of the interacting surface molecules will collect vibrational energy quanta, the so-called excimols. The number of excimols accumulated during the interaction time of at least 1 ps increases with the number of dipoles in the IR-antennas. Excimol energy can be transmitted back to the grazing nanoparticle by a ps-photon flux, which is estimated intense enough to induce multi-ionization of nanoparticle constituents. The resulting charges inside the nanoparticles cause high Coulomb repulsion forces, which will be able to promptly dissociate them.

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1. Introduction

In the last decades, Coulomb dissociation or Coulomb explosion of molecular nanoparticles, e.g. molecular nanoclusters consisting of identical atoms or small molecules ionized by high intensity ps-laser pulses, has been observed [1 – 5]. The analysis of the interaction of an intense laser flux with nanoparticles revealed that their ultrafast multi-ionization is the first step of the process. In the second step the repulsion between two or more atomic groups with positive charges inside the irradiated nanoparticles can lead to prompt dissociation or Coulomb explosion and emission of charged and neutral fragments. In a set of experimental and theoretical works [6 – 11], a general theoretical model of this Coulomb explosion process was suggested and developed. In this model, high intensity ps-laser pulses were described in terms of classical electrodynamics, e.g. as a radiation flux, which is able to interact with the electrons of a nanoparticle constituent. This interaction produces non-resonant multi-ionization of the nanoparticle constituents by emission of electrons and can be separated into two regimes by the Keldysh tunnelling parameter

$$\gamma = (V_{\text{ion}}/2\Phi_{\text{pond}})^{1/2}, \tag{1}$$

where V_{ion} is the ionization potential of a nanoparticle constituent and Φ_{pond} the ponderomotive potential of the laser field, i.e. the average kinetic energy of an electron in this field [3].

In the case of $\gamma > 1$, the ionization can be considered as a process of coherent simultaneous multi-photon absorption by constituents of the nanoparticle. In this region, the energy of the absorbed photons is much higher than the ionization potential V_{ion}. In case of $\gamma \leq 1$, the ionization of nanoparticle constituents by the laser pulse can be considered as a tunnelling process. It was shown that the tunnelling ionization probability [3] is about ten times higher than the ionization probability for the multi-photon absorption process.

The tunnelling multi-ionization process of noble gas atoms inside nanoclusters was investigated using a nanosecond laser with $\lambda = 10\,\mu\text{m}$ [12] and a laser with $\lambda = 1.053\,\mu\text{m}$ [3]. In both experiments, the laser

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intensity was in the range $10^{13}-10^{16}\,\mathrm{W/cm^2}$. Both publications reveal that tunnelling ionization occurs during a femtosecond period, i.e. this ionization process is much faster than the laser pulses, and the irradiated volume of the nanoclusters does not change. The Coulomb repulsion among charged atomic groups inside the nanoclusters can lead to prompt fragmentation or Coulomb dissociation.

For the tunnelling ionization of noble gase nanoparticles, the laser appearance intensity was experimentally established, for which a relatively small number of atomic cations of charge state z appears. The analytical expression for the intensity I_{app} of this appearance flux was given in the form

$$I_{\mathrm{app}} = cI_{\mathrm{ion}}^4/128\pi \mathrm{e}^6 z^2. \tag{2}$$

Here, we propose that prompt Coulomb dissociation of molecular nanoparticles can also happen, when they are grazing along organic surfaces at atomic distances with velocities v_{gr} less than the Bohr velocity ($v_{\mathrm{B}} = 10^8$ cm/s) and give a model for this process. It is based on our previously developed model, which describes the excitation and accumulation of excimols (collective vibrational excitations) in organic molecules or nanoclusters grazing along a surface covered by an organic layer [13–15]. In this grazing molecule excitation model (GME) both, the grazing cations and the surface molecules, contain specific substructures (IR-antennas) consisting of periodically located identical diatomic valence bonds with significant dipole momenta, e.g. hydrocarbon chains $(\mathrm{CH_2})_n$.

The current model shows, however, that for grazing molecular nanoparticles, e.g. fullerenes, their ionization and dissociation can occur, even though only the surface molecules contain IR-antennas. It is essential in this case that the grazing velocity of the nanoparticle is in the interval 10^5-10^7 cm/s, for which the grazing time can be estimated to be in the order of a ps. The distance between the grazing nanoparticle and surface molecules is about 2 Å. Some experimental evidence for the prompt Coulomb dissociation is presented later in this article. For simplicity, we call the grazing nanoparticle from now on just cluster.

2. Theory

We consider the Coulomb dissociation of clusters consisting of identical constituents (atoms or small molecules) without IR-antennas. This type of dissociation is proposed to occur when the clusters are grazing along surfaces covered by organic molecules with IR-antennas.

It was shown earlier in our work [15] that IR-antennas in organic surface molecules experience periodic Coulomb fields produced by a set of screened atomic charges in clusters grazing along the surface. For grazing velocities $v_{\mathrm{gr}} \in (10^5–10^7)$ cm/s, this dynamic process produces a range of Coulomb field frequencies including the harmonic frequency ω_{ex} of collective vibrational excitations (excimols) of the IR-antennas in the surface molecules. The analytical expression for the intensity $F(\omega_{\mathrm{ex}}, v_{\mathrm{gr}})$ of this Coulomb field harmonic was derived using the method given in [15]:

$$\begin{aligned} F = \pi c \omega_{\mathrm{ex}} \alpha^{-3} v_{\mathrm{gr}}^{-1} \cdot Z^2 e^2 [\varepsilon_{\mathrm{ex}} \cdot (h v_{\mathrm{gr}} \cdot \Theta)^{-1} - 1]^2 \\ \cdot [\exp(-2R\Theta)]^2, \end{aligned} \tag{3}$$

where $\Theta = (\omega_{\mathrm{ex}}^2 v_{\mathrm{gr}}^{-2} + 1/\alpha_{\mathrm{eff}}^2)^{1/2}$; c is the light velocity, R the distance between grazing clusters and surface, $Z \cdot e$ denotes charges of identical atoms in a set, α_{eff} is a screening radius of these charges, and a is a distance between the atoms in the set.

In the present model, we assume that the grazing clusters consist of identical constituents. Consequently, any set of screened charges of the clusters produces the same Coulomb field magnitude. Therefore, the excimol excitation probability is the same for all orientations of the cluster in space during the grazing period.

The excimols are delocalized collective vibrational excitations with lifetime τ_{ex} which travel between dipoles in IR-antennas. As shown before [13], the time τ_{tr} of excimols transition in an $(\mathrm{CH_2})_n$-antenna from one dipole to a next one is about 10^{-14} s. Thus, each CH-dipole can be excited N times during $\tau_{\mathrm{gr}} \approx 10^{-12}$ s with $N = \tau_{\mathrm{gr}}/\tau_{\mathrm{tr}}$. The delocalization of excimols leads to their accumulation in IR-antennas during the grazing time, which is shorter than the excimols' lifetime.

The total energy E_K of the maximum number $K_{\max} = N \cdot M \cdot P_{01}$ of excimols accumulated in the IR-antenna is $E_K = K_{\max} \cdot E_{\mathrm{ex}}$, where M is a real number indicating the number of dipoles in the antenna, E_{ex} is the energy of one excimol, and P_{01} is the probability of one excimol excitation in the antenna.

The function P_{01} can be obtain by using (3) in the form

$$P_{01} = 4\pi^2 \omega_{\text{ex}} \left(3h\alpha^3 b v_{\text{gr}}^2 \varepsilon_{\text{ex}} \Theta\right)^{-1} \left[M_{01} \cdot \left(D_0 r_0^{-1}\right) \cdot e^2 Z^2 \left(\varepsilon_{\text{ex}} \cdot (h v_{\text{gr}} \Theta)^{-1} - 1\right)^2 \cdot \exp(-2R\Theta)\right]^2, \tag{4}$$

where M_{01} is a dipole transition matrix element and $(eD_0 r_0^{-1})$ the value of the dipole momentum of one dipole in the antenna.

The accumulated excimol energy can be transferred from C–H-dipoles to a dipole-type trap-bond inside the surface molecule. This energy transfer channel was considered in detail in [16]. The probability of this process depends resonantly on the accumulated excimol energy E_K and has a maximum when E_K coincides with the trap-bond's dissociation energy.

Here, we dwell on another possible channel of the excimols' energy transfer from a surface antenna with many dipoles to the grazing cluster. We consider the transition process of K excimols as a multi-photon emission with flux intensity $I(K)$. This flux interacts with the grazing cluster which leads to its multi-ionization. The excimol energy flux $I(K)$ was defined in the form

$$I(K) = K^6 \omega_{\text{ex}}^4 e^2 M_{01}^2 \sin^2 / 4\pi c^3 r^2. \tag{5}$$

As an example, for the set of numbers $K < 3000$, the calculated function $I(K)$ versus K is presented in Figure 1. Parameters of the calculation are: $\omega_{\text{ex}} = 1.2 \cdot 10^{14}\,\text{s}^{-1}$, $M_{01} = 2.8 \cdot 10^{-18}\,\text{cm}^2$ for the antenna $(\text{CH}_2)_{30}$, and the grazing distance $r = 2$ Å.

The estimation of the probability function per time unit for emission of K excimols from the antenna allows to determine the emission time $\tau_{\text{em}} \approx 10^{-12}$ s. Thus, one can expect that interaction of excimols emitted from surface molecule IR-antennas with constituents of a grazing cluster results in their superfast tunnelling ionization leaving the irradiated object volume unchanged. Coulomb interactions between positively charged atomic groups inside the grazing clusters lead to their repulsion. Kinetic energies of two atomic groups, which experience this Coulomb repulsion, can be calculated by the expression

$$E_{\text{kin}}[\text{eV}] = 14 q_1 q_2 / r_{\text{g}}[\text{Å}], \tag{6}$$

where q_1 and q_2 are the charge values of these groups, and r_{g} is the distance between them. E_{kin} can be high enough to disassemble the grazing species and to produce fragment ions. Therefore it should be possible to verify the Coulomb dissociation process experimentally by time-of-flight mass-spectrometric (TOF-MS) analysis of the fragment ion spectra of grazing clusters.

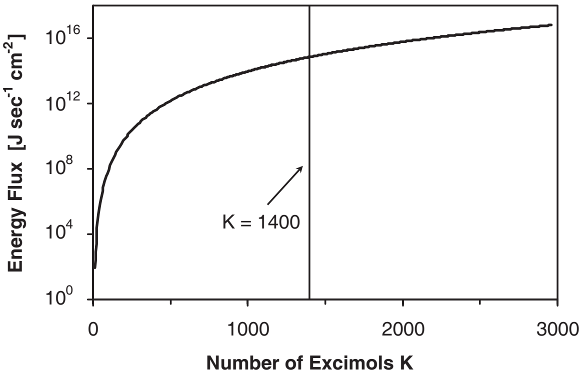

Fig. 1. Energy flux emitted by an antenna $(\text{C}_n\text{H}_{2n})_{30}$ of a surface molecule versus the number K of excimols accumulated in the antenna according to (5).

3. Experiment

To test our Coulomb dissociation model for nanoclusters grazing slowly along organic surfaces, we investigated the dissociation of C_{60}^{+} fullerene ions experimentally. A device was used which was constructed earlier in our mass-spectrometric studies of peptide molecule fragmentation [17]. In this device, C_{60}^{+}-ions were desorbed from a surface by laser pulses with the wave length of 335 nm, then accelerated up to the energy of 8 keV and directed under the angle of 12° to the converter surface. The surface consisted of an aluminized foil covered by mineral oil molecules containing hydrocarbon chains $(\text{CH}_2)_n$, $n \geq 30$ (IR-antennas). By choosing a positive converter foil potential, the C_{60}^{+} ions were grazing along the oil molecules at a velocity of $v_{\text{gr}} = 1.18 \cdot 10^6\,\text{cm}\,\text{s}^{-1}$, corresponding to a kinetic energy of 500 eV at distance $R \approx 2$ Å, without penetration into the converter surface. During the grazing time ($\tau_{\text{gr}} \approx 2 \cdot 10^{-12}$ s), periodic Coulomb fields produced by the set of screened charges of carbon atoms in the grazing fullerene ions can excite excimols in the chained dipoles (C–H) of the surface IR-antenna.

During a time less than the excimol lifetime, the sum energy of the accumulated excimols can be transferred by dipole–dipole interaction either to trap-bonds of the converter oil molecules or to their electronic

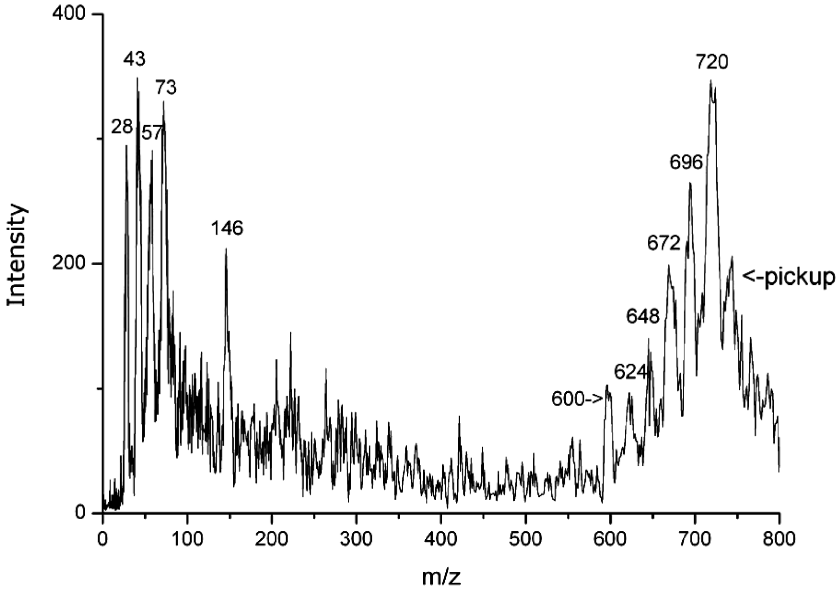

Fig. 2. Molecular fragmentation of grazing C_{60}^{1+} cations; the detected large fragments at m/z 696, 672, 648, 624, and 600 are the singly charged cations C_{58}^{1+}, C_{56}^{1+}, C_{54}^{1+}, C_{52}^{1+}, and C_{50}^{1+}.

trap-bonds. The excimol energy can also leap to the grazing fullerene ions as a photon flux. We note that the latter process is able to induce tunnelling multi-ionization of the carbon atoms located inside the irradiated fullerene ion volume close to the surface. This leads to Coulomb dissociation of the fullerene ions finally.

The dissociated C_{60}^{+}-fragments together with other secondary ions produced during the grazing time were detected by our technique originally named 'grazing incidence surface induced dissociation (GI-SID)' [17]. As this method is not a variance of SID, we renamed the process to 'grazing molecule excitation' resp. 'grazing molecule dissociation' in 2010 [18].

The experimental mass spectrum of dissociated fullerene ions [19] is presented in Figure 2 in the mass range *m/z* 0–800. This spectrum reveals fragment ion peaks at *m/z* 696, 672, 648, 624, and 600 corresponding to the fragment ions C_{58}^{+}, C_{56}^{+}, C_{54}^{+}, C_{52}^{+}, and C_{50}^{+}. This result demonstrates a fast single step elimination of C_{2n} units ($n = 1, 2, 3, 4$, and 5) from C_{60}^{+}. It makes possible to propose, that the dissociation of C_{60}^{+} ions grazing slowly along organic surfaces occurs due to tunnelling multi-ionization and Coulomb repulsion of the ionized carbon atom groups inside the fullerene ion.

To analyse the experimentally observed C_{60}^{+}-ion fragmentation, we follow the procedure in the frame of the presented model. First, we define the highest possible positive charge number $z_{\max}$ which carbon ions can have inside the grazing C_{60}^{+}-ions after irradiation by the photon flux emitted from surface molecule antennas. Second, we calculate the internal kinetic energy which can be produced due to Coulomb repulsion inside the irradiated fullerene ions. Third, we analyse possible C_{2n}-fragments generated by the Coulomb repulsion.

Using (2), the appearance intensity I_{app} of multi-charged carbon atoms in C_{60}-molecules is calculated versus the ionization potential $V_{\text{ion}}(z)$ of single carbon atoms (Fig. 3). The values of $V_{\text{ion}}(z)$ were taken from [20–22].

As it was shown above, we must compare the values of I_{app} with $I(K_{\max})$ to find $z_{\max}$. While the clusters are grazing along organic surfaces, collective vibrational states (excimols) are excited and accumulated in the $(CH_2)_n$-antennas of the surface molecules. Each of the accumulated excimols has the energy 0.07 eV. The excitation probability of one excimol P_{01}, calculated by (4) for $R = 2$ Å, $a = 2$ Å, and $M_{01}^2 = 2.8 \cdot 10^{-18}$ cm^2, has the value $P_{01} = 0.6$. If the mean grazing time τ_{gr} is $2 \cdot 10^{-12}$ s, and the time τ_{tr} of excimol transition to a $(CH_2)_n$-antenna is about $5 \cdot 10^{-14}$ s, the maximum effective number of excimols $K_{\max}$ is 1400. The intensity of the photon flux corresponding to the emission of $K_{\max}$ excimols, calculated by (5), is $I(K_{\max} = 1400) =$

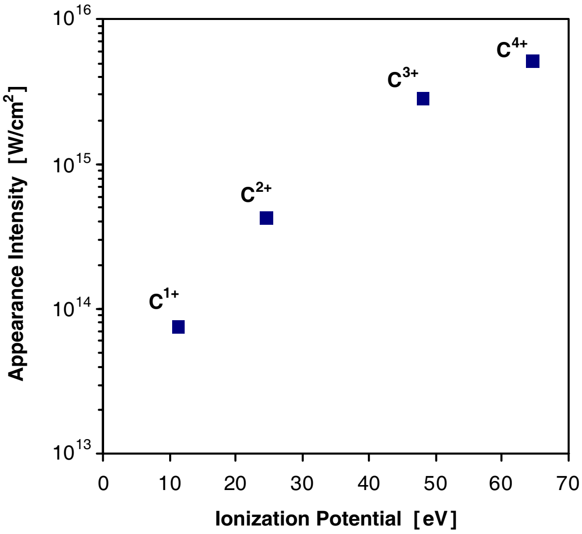

Fig. 3 (colour online). Appearance intensity of multiply charged carbon ions versus ionization potential V_{ion}.

Table 2. Charge split of six C^+-ions into two fragments (binary fission) with the charge q_1 and the resulting kinetic energy after Coulomb dissociation.

Charge split (q_1, q_2) $[e^+]$	(3, 3)	(2, 4)	(1, 5)
$E_{\text{kin}}(q_1, q_2)$ [eV]	65	57	36

$7.5 \cdot 10^{14}$ W/cm². Due to the experimental geometry, this flux can act on approximately 12 carbon atoms inside the irradiated spot at the fullerene surface. Using Dirac's work [23], one can prove that this high intensity photon flux is emitted by an antenna in a short pulse (≈ 1 ps).

By comparison of the appearance flux intensity $I_{\text{app}}(z)$ from Figure 3 with the maximum intensity of the photon flux emitted by an IR-antenna, the relation $I(K_{\max} = 1400) \le I_{\text{app}}(z = 2)$ can be derived. In accordance with the work published in [3], we can conclude that in this case a maximum number of six singly charged carbon atoms are produced inside the fullerene ion and that the number of generated doubly charged carbon atoms is negligible.

This result can also be obtained from the analysis of the number of electrons emitted by the C_{60}^+-ion due to the excimol energy flux $I(K = 1400)$. The fullerene C_{60} must be considered as a molecule with a π-electron system. The ionization potential $V_{\text{ion}}(z)$ as a function of the number of electrons emitted from a fullerene molecule was taken from [20] and is presented in Table 1. By using (2), we calculated the value of $I_{\text{app}}(z)$ as a function of ionization potential $V_{\text{ion}}(z)$. The results are also presented in Table 1. Comparing the flux intensity $I_{\text{app}}(z)$ values from Table 1 with the maximum intensity $I(K_{\max} = 1400)$ of the excimol flux in our experiment, we conclude, that the grazing C_{60}^+-ions can emit up to six electrons during grazing time. These electrons are π-electrons, each of them related to a carbon atom inside the irradiated spot at the fullerene molecule.

The two above presented analyses show that up to six C^+-ions can be produced by the excimol energy flux inside the irradiated volume of the grazing fullerene ion.

The following combinations of six C^+-ions of two-atomic groups C_1, C_2 with positive charges q_1, q_2 inside the grazing fullerene ions are possible: $q_1 = 3^+$, $q_2 = 3^+$ or $q_1 = 2^+$, $q_2 = 4^+$ or $q_1 = 1^+$, $q_2 = 5^+$. The calculated photon irradiation time is about 10^{-12} s. During this short time, the volume of the grazing fullerene ion remains unchanged and therefore the average distance between the charged groups inside the C_{60}^{6+} can be taken as 2 Å. The kinetic energies $E_{\text{kin}}(q_1, q_2)$ of the accelerated carbon atoms of the above mentioned charged atomic groups calculated by (6) are presented in Table 2.

The internal energies $E(n)$, which are needed for the fullerenes' Coulomb dissociation with fragments C_{2n} $(n = 1, 2, 3, 4, 5)$, have the values 30, 36, 42, 48, and 54 eV, correspondingly [24]. The comparison of these values with our calculations for $E_{\text{kin}}(q_1, q_2)$ shows that the here presented model of C_{60}^+ Coulomb dissociation can explain the production of the fullerene fragments C_{58}^+, C_{56}^+, C_{54}^+, C_{52}^+, and C_{50}^+ (Fig. 2) plus charged or neutral fragments C_{2n} $(n = 1, 2, 3, 4, 5)$ [25]. However, in our experiments, we can accelerate and detect exclusively the cations.

z	2	3	4	5	6
$V_{\text{ion}}(z)$ [eV]	11 ± 0.5	21 ± 1	31 ± 2	37 ± 2	42 ± 2
$I_{\text{app}}(z)$ $[10^{14}\ \text{W/cm}^2]$	0.4 ± 0.1	2.2 ± 0.4	5.7 ± 0.7	7.4 ± 1.5	8.6 ± 1.5

Table 1. Ionization potential $V_{\text{ion}}(z)$ and appearance flux intensity $I_{\text{app}}(z)$ as a function of the number z of electrons lost by a grazing fullerene ion.

4. Conclusion

We show in the presented work that Coulomb dissociation of molecular clusters with identical constituents can occur when the clusters are grazing with a velocity less than the Bohr velocity at atomic distances along organic surfaces containing molecules with IR-antennas. Then a grazing molecule excitation (GME) process takes place which accumulates collective vibrational energy quanta (excimols) in the IR-antennas of the affected surface molecules. Partly, the accumulated vibrational energy in the surface molecules is transferred to the grazing clusters by short photon pulses (10^{-12} s) with an intensity of about 10^{14} W/cm^2. This can lead to multi-ionization and finally Coulomb dissociation of the clusters, an effect comparable to the Coulomb dissociation or explosion caused by a high intensity laser pulse in the tunnelling regime [25].

The considered process has been demonstrated experimentally using the example of fullerene cations [19]. When slow C_{60}^{+}-ions (velocity $1.18 \cdot 10^6$ cm/s) are grazing along a planar surface covered by molecules containing nanoscale IR-antennas, the C_{60}^{+}-ions can pick-up some surface excimols in their π-electron system and hence can be multi-ionized in the tunnelling regime [3]. The resulting high charge density eventually causes dissociation of the fullerene ions as described theoretically by the Coulomb dissociation model presented here.

We note that the absence of peaks corresponding to multiply charged fullerene ions C_{60}^{q+} ($q > 1$) in the experimental mass spectrum (Fig. 2) is related to properties of the tunnelling multi-ionization process which is effective in clusters irradiated by a ps-photon flux with an intensity of $10^{-9}-10^{-15}$ W/cm^2. This is in agreement with other experimental results [26, 27].

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