atoms

MDPI

Article

Investigation of Resonance-Enhanced High-Order Harmonics by Two-Component Laser-Produced Plasmas

Jingguang Liang [1,2], Mottamchetty Venkatesh [1], Ganjaboy S. Boltaev [1], Rashid A. Ganeev [1], Yu Hang Lai [1,2,*] and Chunlei Guo [3,*]

[1] GPL, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China; liangjingguang16@mails.ucas.ac.cn (J.L.); venkatesh769@gmail.com (M.V.); boltaev@mail.ru (G.S.B.); ganeev@mail.ru (R.A.G.)
[2] University of Chinese Academy of Sciences, Beijing 100049, China
[3] The Institute of Optics, University of Rochester, Rochester, NY 14627, USA
* Correspondence: laiyh@ciomp.ac.cn (Y.H.L.); guo@optics.rochester.edu (C.G.)

Abstract: Resonance-enhanced harmonics from laser-produced plasma plumes are an interesting phenomenon, whose underlying mechanism is still under debate. In particular, it is unclear whether the macroscopic dispersion properties of the plasma are the key factors for the formation of the enhancement. To shed light on this problem, we perform experiments with two-component plasmas, in which one of the components (tin) is known to be able to generate enhanced harmonics and the other component (lead) is known for altering the overall dispersion properties of the plasma medium. We compare the harmonics spectra from the plasma of pure tin and the plasma of tin/lead alloy. Depending on the driving wavelength, we observe enhanced harmonics at around 47 or 44 nm in both types of plasmas. The two enhanced regions could be attributed to resonances in singly-charged and doubly-charged tin ions, respectively. Our results indicate that the co-existence of lead plasma does not destroy the presence of the enhanced harmonics of tin plasma, and it seems to suggest that the macroscopic properties of the plasma are not the origin of the resonance-enhanced harmonics in tin.

Keywords: high-order harmonic generation; mixed laser-produced plasma; resonance enhancement; two-color pump

check for updates

Citation: Liang, J.; Venkatesh, M.; Boltaev, G.S.; Ganeev, R.A.; Lai, Y.H.; Guo, C. Investigation of Resonance-Enhanced High-Order Harmonics by Two-Component Laser-Produced Plasmas. *Atoms* **2021**, *9*, 1. https://doi.org/10.3390/atoms9010001

Received: 1 December 2020
Accepted: 31 December 2020
Published: 5 January 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

High-order harmonic generation (HHG) is an extreme nonlinear optical process that promises important applications for generating coherent extreme ultraviolet (XUV) radiation [1–5] and detecting ultrafast dynamics of atomic, molecular, and solid systems [6,7]. However, a major shortcoming, which limits the applicability of HHG, is the low conversion efficiency. Although gases have been the most commonly used HHG medium, there are very limited kinds of elements to choose. Instead, the laser-produced plasma (LPP) from solid surface is an attractive alternative for HHG, which can be produced during the process of laser-induced surface structure [8,9]. This method can be applied to various type of solid samples [10–12]. The conditions for the effective emission of coherent XUV radiation by laser pulses in plasma produced on the surfaces of different materials have been extensively studied [13–17]. Previous discussions on multiphoton resonance in HHG have involved, in particular, the resonance excitation of bound states [18,19]. In particular, the resonance enhancement of specific harmonics found in some materials could lead to an increase in the conversion efficiency [20–22] by more than an order of magnitude as compared with the neighboring harmonics.

Various theoretical studies have provided explanations for harmonic enhancement caused by resonance [23–27]. In the case of plasma HHG, the improvement of harmonic efficiency due to the autoionization resonance process was proposed by Strelkov [25], and this method seemed to have considerable prospects in the use of ion resonance and atomic

resonance in some cases. However, there are two competing proposed mechanisms on how the resonance contribute to the enhancement in harmonics yield; one mechanism is based on a single-atom response [25,28,29], and the other mechanism is related to the macroscopic phase matching effect [30,31].

If macroscopic phase matching effect is, indeed, the origin of the enhanced harmonics, it is reasonable to expect that the enhancement should be destroyed if the plasma composition, and thus the dispersion properties, is altered. Therefore, it is illustrative to study harmonics from a mixed plasma in which one of the components is known to give resonance-enhanced harmonics while the other component does not. In this paper, we study HHG from LPP of tin (Sn), lead (Pb), and the alloy (Pb-Sn) of them. Sn plasma is one of the well-known species which exhibits resonance-enhanced harmonics. The transition $4d^{10}5s^25p^2P_{3/2}$-$4d^95s^25p^2$ (^{1}D) $^2D_{5/2}$ of Sn^+ contributes to an enhancement at the wavelength of 47.06 nm (the 17th order under the driving wavelength of 800 nm) [32]; the transition $4d^{10}5s5p$ $(1/2, 3/2)_2$-$4d^95s5p^2$ $(5/2,1/2)_3$ of Sn^{2+} contributes to an enhancement at a wavelength of 44.44 nm (the 18th order under the driving wavelength at 800 nm) [33]. In addition, it is known that Pb does not show any enhanced harmonics with our driving wavelength. We will consider the following two cases: the first case is with 800 nm driving pulse (single-color pump (SCP)), and the second case is with a superposition of 800 nm and 400 nm driving pulses (two-color pump (TCP)).

Our results indicate that the co-existence of Pb plasma does not significantly affect the presence of the enhanced harmonics of Sn plasma, which seems to suggest that the macroscopic properties of the plasma is not the origin of the enhancement.

2. Experimental Setup

The schematic of our experimental setup is shown in Figure 1. In these experiments, a driving pulse (DP) is used to generate harmonics through the interaction with the plasma plume pre-formed by a heating pulse (HP), which is either an uncompressed picosecond pulse (800 nm, 200 ps, 100 Hz) or a femtosecond pulse (800 nm, 35 fs, 100 Hz). The other part of femtosecond pulse is used as the DP, which arrives at the plasma plume at about 70–80 nanoseconds after HP ablated the sample surface. The HP is focused by a 200 mm focal length spherical lens (SL2), while the DP focusing uses a 500 mm focal length spherical lens (SL1). The position of the targets regarding the optical axis of the DPs and focal plane of the focusing lens is changed using the three-coordinate translating stage. The harmonic yield is maximized when the distance between the target and the axis of DP propagation is set at ~150 µm. The diameter of focused driving femtosecond pulses is measured to be ~85 µm, with a Rayleigh length of about 7 mm. The DP energy used in this study is fixed at 0.6 mJ, considering the various effects during the process of propagation, the pulse duration should change from 35 fs to 50 fs, and therefore the DP intensity is calculated to be ~4×10^{14} W/cm^2. After passing through the entrance slit of the spectrometer (XUV chamber), first, the harmonics radiation is reflected by a cylindrical mirror onto a 1200 grooves/mm flat field grating, and then the dispersed harmonics are enhanced by a micro-channel plate (MCP) and viewed by the phosphor screen to be available to be captured by a CCD camera. In order to study the effect of TCP of LPP on the high-order harmonics yield, a 0.2 mm thick β-barium borate (BBO) crystal is mounted on an independent translation stage between the spherical lens and target.

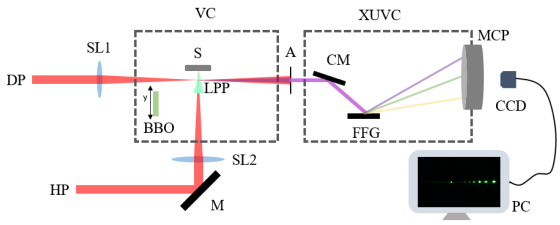

Figure 1. Schematics of experimental setup. DP, driving pulse; HP, heating pulse; SL1, spherical lens with a 500 mm focal length; SL2, spherical lens with a 200 mm focal length; BBO, 0.2 mm thick type I

beta barium borate crystal; M, mirrors; S, samples; LPP, laser-produced plasma; VC, target vacuum chamber; XUVC, coherent extreme ultraviolet (XUV) vacuum chamber; A, slit; CM, cylindrical mirror; FFG, flat field grating; MCP, micro-channel plate; CCD, CCD camera; PC, personal computer.

3. Results and Discussion

Figure 2 shows the high-order harmonic distribution generated in the plasmas produced on the surface of Pb, Sn, and Pb-Sn alloy targets, represented by red, green, and blue lines, respectively. These results are obtained from plasmas performed by femtosecond (upper panels) and picosecond (bottom panels) HPs. One can see the difference between these results from different samples, while there have little difference between different HPs. The most significant difference between these three samples is that the resonant enhanced 17th harmonic from the Sn plasma plume, which is much higher than the neighbor harmonics, which has also been reported by many works [16,34]. The strong 17th harmonic is enhanced by a strong transition $4d^{10}5s^25p^2P_{3/2}$-$4d^95s^25p^2$ (^{1}D) $^2D_{5/2}$ of Sn^+ [32]. In the case of Pb, the harmonic distribution is smooth overall, no clear enhanced harmonics is observed, as expected. The results of Pb-Sn alloy, although being quite different from the results of Pb and Sn, indicate that the enhancement of the 17th order remains. For example, in the case of femtosecond HP, the yield ratio between the 17th and 19th order is about 5, which is just slightly less than the case of pure Sn plasma, while the ratio of the 17th and 15th order reduces to 2 in mixed plasma, as compare with that of 4 in Sn plasma.

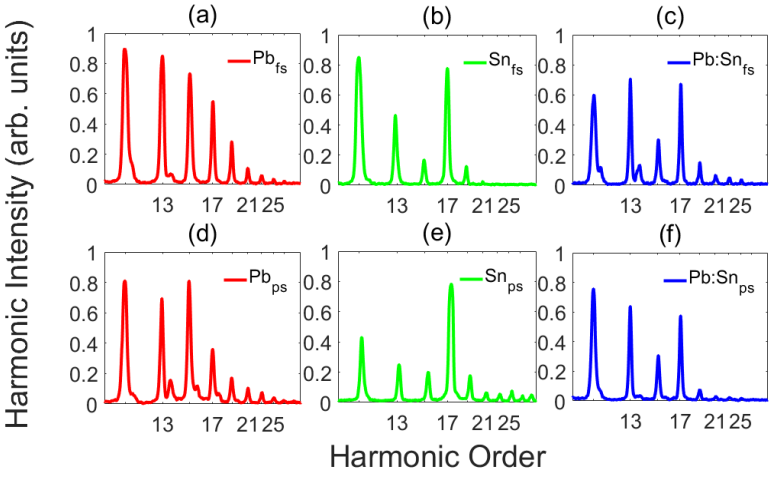

Figure 2. Spectral distributions of the harmonics generated in Pb (red lines), Sn (green lines) and Pb-Sn alloy (blue lines) plasmas produced by 800 nm, 35 fs, 100 Hz (upper panels) and with 800 nm, 200 ps, 100 Hz (lower panels) heating pulses. All vertical axes are in linear scale.

In the case of TCP driving, the polarizations of the two waves (800 nm and 400 nm) are orthogonal to each other. Note that there is a delay of 38fs between them due to the group velocity dispersion in the 0.2 mm BBO crystal [35]. The BBO crystal that was placed 40 cm from the focusing lens led to a conversion efficiency of the second harmonic (SH) of about 10% under the intensity of the DP we used. The focused beam area of 800 nm is 2.5 times that of the 400 nm beam area, and therefore the intensity of the 800 and 400 nm waves is at a ratio of 3.6:1, which leads to a SH intensity of about 9×10^{13} W/cm^2. According to the cut-off energy formula $E = I_P + 3.17U_P$ [36,37] (where I_P is the ionization potential; $U_P = 9.33 \times 10^{-14} I(W/cm^2)\lambda^2(\mu m)$ is the ponderomotive potential, in which I is the laser intensity; and λ is the wavelength of incident laser), the cut-off energy from Sn^+ (with a ionization potential at 14.63 eV) and Pb^+ (with a ionization potential at 15.03 eV) in the case of SH driving pulse are calculated to be 18.89 eV and 19.29 eV, respectively, corresponding to a harmonic order of around 12, which means that we cannot get harmonics more than 12th, with SH alone.

Figure 3 shows the comparison of the harmonic spectra generated from SCP and TCP. In the case of TCP, even harmonics arise due to the break of symmetry [38]. In addition, some odd harmonics become weaker as compared with the case of SCP. As the results generated from TCP shown in Figure 3, we observe spectra with both even and odd harmonics, with a large variation among different orders. First, a resonance-enhanced 18th harmonic arises, and such enhancement has been attributed to a resonance transition $4d^{10}5s5p\ (1/2,\ 3/2)_2$-$4d^9 5s5p^2\ (5/2,\ 1/2)_3$ of Sn^{2+}, as discussed in [33]. The harmonics appear with a special intensity distribution, which is that, in addition to the resonant-enhanced 18th harmonic, the 2(2n+1)th harmonics are also much stronger than the others. Actually, the enhancement of the 2(2n+1)th orders has been confirmed in gas medium [39], and such enhancement pattern only occurred if the two driving fields overlapped well in time. In the case of Pb plasma, however, only the 10th and 14th harmonics are stronger, and the 18th and 22th harmonics are out of sight. When it comes to the mixed plasma, a clear enhanced 10th, 14th and 18th harmonics appear, and the 22th harmonic also appears. It is notable that the 18th harmonic is still very strong, and it seems that the additional component (Pb) does not play a significant role.

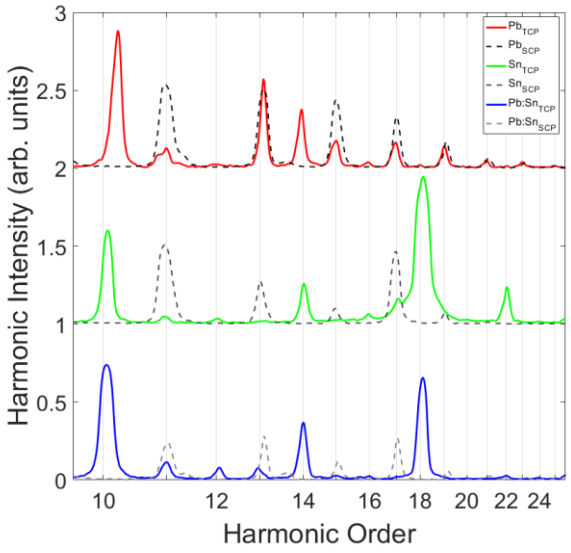

Figure 3. Two-color pump (TCP, solid lines) and single-color pump (SCP, dotted lines) spectral distributions of the harmonics generated from Pb (**upper panel**); Sn (**middle panel**); and Pb-Sn alloy (**bottom panel**) plasmas, with 800 nm, 35 fs, 100 Hz heating pulse. Vertical axis is in linear scale. For visibility, the three sets of spectra are displaced vertical from each other.

It is clear that the 17th and 18th harmonics should be resonant enhanced [16,33,34] under SCP and TCP pulses. Meanwhile, we need to consider why resonance enhancement also occurs in mixed plasmas. From both SCP and TCP results in Figures 2 and 3, one can clearly find that both components play some roles in harmonic generation, for example, in the results generated from mixed plasma, the appearance of the resonant harmonic indicates the existence of tin, while the variation of the relative intensity between resonance harmonic and the neighbors confirms the existence of lead. It is reasonable to anticipate that the mixing of two components will inevitably lead to a change in the plasma dispersion properties, and thus the phase matching condition. Therefore, the fact the enhanced harmonics survive seems to suggest that phase matching is not the origin of the enhancement.

4. Conclusions

We have demonstrated that high-order harmonics can be generated effectively from Pb, Sn, and their alloy plasmas during propagation of femtosecond SCP and TCP pulses. The emphasis of this study is to observe and analyze the resonant harmonics in the

case of the plasmas containing different emitters and their mixtures. In the case of SCP, a resonance-enhanced 17th (47.06 nm) harmonic is observed from pure Sn plasma, as well as from mixed Sn and Pb plasma. When TCP was applied, a significant effect on improving the harmonic field occurred and also a resonantly enhanced 18th harmonic in both Sn and mixed plasmas was generated. The hybrid scheme provides the possibility for understanding the mechanism of the resonant harmonics. Our results seem to indicate that the macroscopic properties of the plasma are not the origin of the enhancement.

Author Contributions: J.L. and M.V. performed the experiments; J.L. performed the data analysis and writing of the original draft; Y.H.L., R.A.G., and G.S.B. provided supervision; C.G. and Y.H.L. performed the review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (2018YFB1107202, 2017YFB1104700), the National Natural Science Foundation of China (91750205, 12004380), the Strategic Priority Research Program of Chinese Academy of Sciences (XDA22010302), and the K. C. Wong Education Foundation (GJTD-2018-08).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Krausz, F.; Ivanov, M. Attosecond physics. *Rev. Mod. Phys.* **2009**, *81*, 163. [CrossRef]
2. Hentschel, M.; Kienberger, R.; Spielmann, C.; Reider, G.A.; Milosevic, N.; Brabec, T.; Corkum, P.; Heinzmann, U.; Drescher, M.; Krausz, F. Attosecond metrology. *Nature* **2001**, *414*, 509–513. [CrossRef] [PubMed]
3. Witte, S.; Tenner, V.T.; Noom, D.W.; Eikema, K.S. Lensless diffractive imaging with ultra-broadband table-top sources: From infrared to extreme-ultraviolet wavelengths. *Light Sci. Appl.* **2014**, *3*, e163. [CrossRef]
4. Hädrich, S.; Krebs, M.; Hoffmann, A.; Klenke, A.; Rothhardt, J.; Limpert, J.; Tünnermann, A. Exploring new avenues in high repetition rate table-top coherent extreme ultraviolet sources. *Light Sci. Appl.* **2015**, *4*, e320. [CrossRef]
5. Kanda, N.; Imahoko, T.; Yoshida, K.; Tanabashi, A.; Eilanlou, A.A.; Nabekawa, Y.; Sumiyoshi, T.; Kuwata-Gonokami, M.; Midorikawa, K. Opening a new route to multiport coherent XUV sources via intracavity high-order harmonic generation. *Light Sci. Appl.* **2020**, *9*, 1–9. [CrossRef]
6. Uiberacker, M.; Uphues, T.; Schultze, M.; Verhoef, A.J.; Yakovlev, V.; Kling, M.F.; Rauschenberger, J.; Kabachnik, N.M.; Schröder, H.; Lezius, M. Attosecond real-time observation of electron tunnelling in atoms. *Nature* **2007**, *446*, 627–632. [CrossRef]
7. Wang, D.; Zhu, X.; Liu, X.; Li, L.; Zhang, X.; Lan, P.; Lu, P. High harmonic generation from axial chiral molecules. *Opt. Express* **2017**, *25*, 23502–23516. [CrossRef]
8. Vorobyev, A.Y.; Guo, C. Direct femtosecond laser surface nano/microstructuring and its applications. *Laser Photonics Rev.* **2013**, *7*, 385–407. [CrossRef]
9. Fang, R.; Vorobyev, A.; Guo, C. Direct visualization of the complete evolution of femtosecond laser-induced surface structural dynamics of metals. *Light Sci. Appl.* **2017**, *6*, e16256. [CrossRef]
10. Bom, L.E.; Kieffer, J.-C.; Ganeev, R.; Suzuki, M.; Kuroda, H.; Ozaki, T. Influence of the main pulse and prepulse intensity on high-order harmonic generation in silver plasma ablation. *Phys. Rev. A* **2007**, *75*, 033804.
11. Bom, L.E.; Haessler, S.; Gobert, O.; Perdrix, M.; Lepetit, F.; Hergott, J.-F.; Carré, B.; Ozaki, T.; Salières, P. Attosecond emission from chromium plasma. *Opt. Express* **2011**, *19*, 3677–3685.
12. Fareed, M.; Mondal, S.; Pertot, Y.; Ozaki, T. Carbon molecules for intense high-order harmonics from laser-ablated graphite plume. *J. Phys. B At. Mol. Opt. Phys.* **2016**, *49*, 035604. [CrossRef]
13. Bom, L.E.; Pertot, Y.; Bhardwaj, V.; Ozaki, T. Multi-μJ coherent extreme ultraviolet source generated from carbon using the plasma harmonic method. *Opt. Express* **2011**, *19*, 3077–3085. [CrossRef] [PubMed]
14. Fareed, M.; Strelkov, V.; Singh, M.; Thiré, N.; Mondal, S.; Schmidt, B.; Légaré, F.; Ozaki, T. Harmonic generation from neutral manganese atoms in the vicinity of the giant autoionization resonance. *Phys. Rev. Lett.* **2018**, *121*, 023201. [CrossRef] [PubMed]
15. Fareed, M.; Strelkov, V.; Thiré, N.; Mondal, S.; Schmidt, B.; Légaré, F.; Ozaki, T. High-order harmonic generation from the dressed autoionizing states. *Nat. Commun.* **2017**, *8*, 1–5. [CrossRef]
16. Haessler, S.; Strelkov, V.; Bom, L.E.; Khokhlova, M.; Gobert, O.; Hergott, J.-F.; Lepetit, F.; Perdrix, M.; Ozaki, T.; Salières, P. Phase distortions of attosecond pulses produced by resonance-enhanced high harmonic generation. *New J. Phys.* **2013**, *15*, 013051. [CrossRef]

17. Rosenthal, N.; Marcus, G. Discriminating between the role of phase matching and that of the single-atom response in resonance plasma-plume high-order harmonic generation. *Phys. Rev. Lett.* **2015**, *115*, 133901. [CrossRef]
18. Amusia, M.Y.; Connerade, J. The theory of collective motion probed by light. *Rep. Prog. Phys.* **2000**, *63*, 41. [CrossRef]
19. Keller, F.; Lefebvre-Brion, H. Shape resonances in photoionization of diatomic molecules: An example in the d inner shell ionization of the hydrogen halides. *Z. Phys. D At. Mol. Clust.* **1986**, *4*, 15–23. [CrossRef]
20. Ganeev, R.A. Generation of high-order harmonics of high-power lasers in plasmas produced under irradiation of solid target surfaces by a prepulse. *Physics-Uspekhi* **2009**, *52*, 55. [CrossRef]
21. Suzuki, M.; Baba, M.; Kuroda, H.; Ganeev, R.A.; Ozaki, T. Observation of single high-harmonic enhancement by quasi-resonance with a tellurium ion in a laser-ablation plume at 29.44 nm. *JOSA B* **2007**, *24*, 2686–2689. [CrossRef]
22. Ganeev, R.; Odžak, S.; Milošević, D.; Suzuki, M.; Kuroda, H. Resonance enhancement of harmonics in metal plasmas using tunable mid-infrared pulses. *Laser Phys.* **2016**, *26*, 075401. [CrossRef]
23. Frolov, M.; Manakov, N.; Starace, A.F. Potential barrier effects in high-order harmonic generation by transition-metal ions. *Phys. Rev. A* **2010**, *82*, 023424. [CrossRef]
24. Gaarde, M.B.; Schafer, K.J. Enhancement of many high-order harmonics via a single multiphoton resonance. *Phys. Rev. A* **2001**, *64*, 013820. [CrossRef]
25. Strelkov, V. Role of autoionizing state in resonant high-order harmonic generation and attosecond pulse production. *Phys. Rev. Lett.* **2010**, *104*, 123901. [CrossRef] [PubMed]
26. Miroshnichenko, A.E.; Malomed, B.A.; Kivshar, Y.S. Nonlinearly PT-symmetric systems: Spontaneous symmetry breaking and transmission resonances. *Phys. Rev. A* **2011**, *84*, 012123. [CrossRef]
27. Zeng, Z.; Li, R.; Cheng, Y.; Yu, W.; Xu, Z. Resonance-enhanced high-order harmonic generation and frequency mixing in two-color laser field. *Phys. Scr.* **2002**, *66*, 321. [CrossRef]
28. Milošević, D. High-energy stimulated emission from plasma ablation pumped by resonant high-order harmonic generation. *J. Phys. B At. Mol. Opt. Phys.* **2007**, *40*, 3367. [CrossRef]
29. Redkin, P.; Kodirov, M.; Ganeev, R. Theoretical investigation of resonant nonperturbative high-order harmonic generation in indium vapors. *Josa B* **2011**, *28*, 165–170. [CrossRef]
30. Kulagin, I.A.; Usmanov, T. Efficient selection of single high-order harmonic caused by atomic autoionizing state influence. *Opt. Lett.* **2009**, *34*, 2616–2618. [CrossRef]
31. Kulagin, I.Y.A.; Kim, V.V.; Usmanov, T. Compensation for phase mismatch of high harmonics by the group-velocity mismatch. *Quantum Electron.* **2011**, *41*, 801. [CrossRef]
32. Duffy, G.; van Kampen, P.; Dunne, P. 4d→5p transitions in the extreme ultraviolet photoabsorption spectra of Sn II and Sn III. *J. Phys. B At. Mol. Opt. Phys.* **2001**, *34*, 3171. [CrossRef]
33. Ganeev, R.A.; Strelkov, V.V.; Hutchison, C.; Zaïr, A.; Kilbane, D.; Khokhlova, M.A.; Marangos, J.P. Experimental and theoretical studies of two-color-pump resonance-induced enhancement of odd and even harmonics from a tin plasma. *Phys. Rev. A* **2012**, *85*, 023832. [CrossRef]
34. Suzuki, M.; Baba, M.; Ganeev, R.; Kuroda, H.; Ozaki, T. Anomalous enhancement of a single high-order harmonic by using a laser-ablation tin plume at 47 nm. *Opt. Lett.* **2006**, *31*, 3306–3308. [CrossRef] [PubMed]
35. Ganeev, R.A.; Boltaev, G.S.; Stremoukhov, S.Y.; Kim, V.V.; Andreev, A.V.; Alnaser, A.S. High-order harmonic generation during different overlaps of two-colored pulses in laser-produced plasmas and gases. *Eur. Phys. J. D* **2020**, *74*, 1–9. [CrossRef]
36. Corkum, P.B. Plasma perspective on strong field multiphoton ionization. *Phys. Rev. Lett.* **1993**, *71*, 1994. [CrossRef]
37. Kulander, K.; Schafer, K.; Krause, J. Dynamics of short-pulse excitation, ionization and harmonic conversion. In *Super-Intense Laser-Atom Physics*; Springer: Berlin/Heidelberg, Germany, 1993; pp. 95–110.
38. Perry, M.D.; Crane, J.K. High-order harmonic emission from mixed fields. *Phys. Rev. A* **1993**, *48*, R4051. [CrossRef]
39. Kim, I.J.; Kim, C.M.; Kim, H.T.; Lee, G.H.; Lee, Y.S.; Park, J.Y.; Cho, D.J.; Nam, C.H. Highly efficient high-harmonic generation in an orthogonally polarized two-color laser field. *Phys. Rev. Lett.* **2005**, *94*, 243901. [CrossRef]