Spectroscopy of laser-induced autoionizing nonlinear resonances in atomic systems

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Abstract. Efficient harmonic generation at laser-induced autoionizing state in continuum, were observed for the first time by our laboratory [1,2,3]. In this paper, nonlinear frequency mixing in alkali metal vapors at induced continuum structure in Na, are studied in detail. Besides, measurement of nonlinear optical susceptibility at induced autoionizing resonance, is performed. Tunable ultraviolet radiations by four-photon processes near induced resonances are obtained. Estimations of the real and imaginary parts of the nonlinearities, are estimated. We will specially note, that the resonant photoabsorption of ions is experimentally investigated since it gives information about the autoionizing states, which is impossible to obtain on the base only of the emission spectra. We use also laser inducing for obtaining of powerful radiation source in VUV. Thus, many actual problems as the selective impact on matter, laser photochemistry and laser isotope separation are connected directly with the induced autoionizing nonlinear resonances. The main interest is to control the spectral characteristics of continuum. The discrete level from the continuum structure leads to appearance of asymmetrical autoionizing resonance onto the background of the broad-band absorption line.

1. Introduction
First observation of quite efficient nonlinear frequency conversion when the levels of Fano type are laser-induced in continuum, are reported by our laboratory [1,2,3]. We should note, that this possibility of inducing a continuum structure, by laser field coupling with a lower lying bound state, was theoretically predicted in [4,5,6]. If the continuum structure is induced [5], then the photoexcitation rate can be greatly enhanced and such resonant structure becomes important [5] under strong laser field excitation. According to the experimental study [1], a gain of the output THG (third harmonic generation) is much more times efficient due to the induced nonlinear optical resonances in continuum.

It is important, that the bound state coupled to the continuum by the intense radiation field, behaves as an autoionizing state [5], when modifying with a narrow structure the photoionization spectrum. According to theoretical predictions [4,5], the atomic excitations of the photoionization spectra leads to quantum interference of transitions to the continuum from various Rydberg states, which gives highly excited atoms above the ionization potential, with the enhancement of laser-inducing field intensity. The induced autoionizing states in atoms can precisely control the photoionization rate by
an external electromagnetic coherent field, which intensity and frequency can be varied. When the continuum is structured by induced autoionizing state, it is possible to obtain high efficiency of the nonlinear optical processes in atomic systems. Concerning the first experimental evidence of induced autoionizing state, we can characterize this process of efficient tripling [1] – as resonant third harmonic generation in sodium. The experimental research of autoionizing-like states can also require a measurement of other atomic properties such as the birefringence, the dichroism, and especially the efficiency of harmonics generation, which can be tested experimentally. Measurement of the optical polarization rotation in cesium at the induced autoionizing state was obtained in [7], Cs. Considerable efforts were devoted to the direct observation of induced autoionizing states in alkali metal atoms, even due to photoionization of molecules (Na$_2$) [8]. Experimental evidence of induced continuum structure was obtained also in the vicinity of an autoionizing state in rare gases [9].

We can consider, that after the first experimental confirmation of high efficient third harmonic generation [1] near laser-induced autoionizing (AI) state, such strongly resonant phenomena were consequently obtained in a number of coherently excited atomic systems. Our conclusion, is that due to the first experimental efforts – it was created indeed a new quite active scientific field as Resonant Autoionization Laser Spectroscopy. Recently, the experimental study in this new field continue for the continuum structure in different gases [9], atoms etc. An observation of induced autoionizing state in [9] was possible when using the process of multiphoton ionization. Obtaining of the induced autoionizing structure via coherent electromagnetic field was realized by extensive experimental study in various atoms during the last years. These experimental attempts demonstrate also the interference character of laser-induced autoionizing state. As a result, the line shape becomes dependent on the temporal and spatial intensity distribution – of the inducing laser. Further, following the results of experiments in [10], we consider that we can perform coherent amplification without inversion of population. Thus, near induced continuum structure, the inversionless amplification and a lasing is efficient [10], and it is for example favorable for short-wavelength lasing systems in ultraviolet (UV) and VUV region.

In this paper, we investigate four-photon frequency mixing in sodium vapor $2\omega_d + \omega_d' = \omega_s$ near laser-induced AI resonance. The optical mixing efficiency increases, when the dye laser frequency $\omega_d$ corresponds to the two-photon 3s-5s transition in sodium.

2. Experimental setup

We used in our experiment a dye laser with two output frequencies $\omega_d$ and $\omega_d'$, pumping by second harmonic of N$_2$ glass laser. Powerful fundamental laser radiation of $\omega_1$ frequency couples the 10s level (Fig. 1) to the continuum of Na. The experimental setup is given in Fig. 1.

![Figure 1. Energy diagram of optical frequency mixing in sodium at induced resonance from 10s level to E_i state in the continuum.](image)
We use a mode-selector within the cavity of mode-locked Nd\(^{3+}\):glass laser and ensures narrowing of the output linewidth to a magnitude of \(\Delta \nu_1 \leq 0.1 \text{ cm}^{-1}\). The train consists of 10 laser pulses of 2ns duration each. Second harmonic generation \(\omega_2\) is of 30% efficiency in KDP crystal and it is used to pump the dye laser. Dye laser contains a solution of Rhodamine 6GDN, B,F3B in ethanol. The dye laser has two output frequencies \(\omega_d\) and \(\omega_d'\) which are tunable independently using TF-17 grating and two mirrors \(M_d, M'_d\). The output pulses of dye laser are 2 ns long. The dye laser linewidths are \(\Delta \nu_d, \Delta \nu_d' \leq 0.1 \text{ cm}^{-1}\). As it is shown in Fig. 2, part of the fundamental \(\omega_1\) radiation enters in Na cell collinearly with both dye laser \(\omega_d, \omega_d'\) beams.

\[\text{Figure 2. Experimental setup.}\]

1 – photodetectors; 2 – DMR-4 monochromator; 3 – Na cell; M, M\(_d\), M\(_d'\) - mirrors; 4 – dye cell; 5 – grating TF-17; 6 – KDP crystal; 7 – Nd\(^{3+}\):glass laser.

The radiations \(\omega_1, \omega_d, \omega_d'\) are focused into the Na cell by a 30 cm focal length lens. A sodium vapor pressure of 5 Torr is used at \(T = 441^\circ\text{C}\) temperature in order to avoid influence of the absorption coefficient. The signal \(\omega_s\) wave of the optical mixing is obtained in cell of sodium vapor and xenon. The \(\omega_s\) radiation is separated by double monochromator DMR-4 and it is registered by photodetector system.

3. Results

The effect of the Al state induced by \(\omega_1\) beam is studied in this work. The results are compared in case of the \(\omega_1\) radiation absence (i.e., no inducing of AIS), and in case of collinear irradiation of Na cell by all frequencies \(\omega_d, \omega_d'\) and \(\omega_1\). When the dye wavelength are \(\lambda_d = 602.3\ \text{nm}\) and \(\lambda_d' = 615.8\ \text{nm}\), then we have precise coincidence of \(2\omega_d\) with the two-photon transition, and \(\omega_d'\) corresponds to the transition into continuum. The dependence of the signal intensity \(I_s\) versus \(\nu_s\) frequency is presented in Fig. 3. Measurements are made when the phase-matching is fulfilled, and the \(\omega_1\) frequency corresponds to the transition from \(10s\) state to \(E_i\) level in continuum (Fig. 1). Near the induced AIS, the \(I_s\) intensity increases of the order of magnitude. When the nonlinear interaction is not phase-matched, the efficiency is \(\eta = P_s/P_d \sim 10^6\). When the dye laser frequency \(\omega_d\) exactly coincides with the two-photon transition in sodium, the efficiency increases up to \(10^5\). If we have a phase-matching in a mixture of Na vapor and Xe, the measured maximum efficiency is \(2 \times 10^4\).
We used in experiment maximum intensities $I_d$, $I_d'$, and then we can reach also maximum for the $I_s$ signal, but under these conditions we observed the saturation effect.

**Figure 3.** Signal intensity $I_s$ in frequency mixing process as a function of $v_s$, at induced autoionizing resonance.

Dependence of $I_s$ upon $I_d$ and $I_d'$, is presented in Fig. 4. Concerning the fundamental radiation intensity $I_1$, we keep it constant, and the saturation is evident for signal $I_s$ - versus both dye laser output intensities $I_d$, $I_d'$ (Fig.4).

**Figure 4.** Dependence of signal $I_s$ upon the dye laser outputs $I_d$ (curve 1), $I_d'$ (curve 2,) and observation of the saturation effect.

Laser-induced autoionizing state leads to great efficiency of harmonic generation and of nonlinear conversion processes, but it is also important to examine the ionization and to measure the ionization yield when scanning the tunable frequency via resonance. Then, the experimental setup consists of a time-of-flight mass-spectrometer, in which the Na atoms are introduced in the form of an effusive beam. The beams of two tunable dye lasers $\omega_d$, $\omega_d'$ of 0.2 cm$^{-1}$ bandwidth are combined in a
dichroic mirror and cross the atomic beam, focused with a 15 cm achromatic lens. The ionized species are extracted with a dc electric field at right angles with respect to the atomic and laser beams through a 2-mm-diameter aperture in front of which the two laser beams are focused, so that only ions produced at the focus could reach the microchannel plate detector.

**Figure 5.** Ionization spectrum of sodium scanning $\lambda_d$ in the range 601.0 – 602.8 nm and exactly on laser-induced autoionizing resonance coupling 10s level to the continuum.

A summary of the main experimental results is given in Fig. 5 and Fig. 6. The Fig. 5 – 6 show a scan of the wavelength $\lambda_d$ between 601.0 nm and 602.8 nm, and two resonances are detected, correspondingly.

The peak at 602.3 nm corresponds to the two-photon resonant ionization of Na when $2\omega_d$ coincides precisely with $3s - 5s$ two-photon transition in sodium. The second peak of the intensity in Fig. 5 appears only when the fundamental $\omega_1$ laser beam is introduced and we have induction of autoionizing resonance as a continuum structure near 601.9 nm (Fig. 5).

As it is evident from Fig. 6, following our experimental results with mass analysis of the ions, we have only one peak of the ionization yield at the two-photon $3s - 5s$ transition; i.e., there is no in this case an inducing of autoionizing resonance and the dependence in Fig. 6 is obtained for the absence of $\omega_1$ radiation in front of Na atoms. As it is demonstrated on Fig. 5, the asymmetry is evident in the observed laser-induced continuum structure when measuring the ionization yield spectra.

The ability to introduce additional tunable resonance in the nonlinear optical susceptibility of sodium (Fig. 5) by the injection of a radiation $\omega_1$ field is an attractive possibility in order to obtain an efficient optical frequency mixing process. Such effective nonlinear conversion at an induced autoionizing state is possible with an enhancement more than order of magnitude of the signal $\omega_s$ wave within the frequency mixing $2\omega_d + \omega_d' = \omega_s$ process in sodium. At the same time, the dye laser $2\omega_d$ frequency corresponds to two-photon $3s - 5s$ transition in the atomic Na system. Since we use the induced autoionizing resonance and we involve two-photon $3s - 5s$ transition as well (Fig. 5), then we apply two dye laser $\omega_d$, $\omega_d'$ frequencies and the fundamental $\omega_1$ beam in Na atoms. The result of inducing the autoionizing state verify the significance of modification of the atomic system with a continuum structure, and we obtain greater $\omega_s$ efficiency.
Figure 6. Ionization yield of Na when tuning the $\lambda_d$ within the region 601.0 – 602.8 nm, but without using of $\omega_1$ fundamental beam and there is no induced autoionizing resonance under these conditions.

We study frequency mixing when using collinearly dye laser $\omega_d$, $\omega_d^*$ and the $\omega_1$ beams for enhancement of the signal $\omega_s$ wave by a direct fifth-order nonlinear mixing process. We will establish conclusively that the increasing of frequency mixing efficiency arises first of all from a resonance in the nonlinear optical susceptibility. The optical frequency mixing is described by direct and cascade six-photon processes. The direct process corresponds to the nonlinear optical susceptibility.

$$\chi^{(5)}(\omega_s; \omega_d, \omega_d^*, \omega_1, -\omega_1)$$

nonlinear optical susceptibility. We consider, that the cascade six-photon interaction consists of two successive four-photon processes. The interaction $2\omega_d + \omega_d^* = \omega_s$ determines the frequency mixing. Second cascade process is of the two-photon Raman amplification type which corresponds to the $\chi^{(3)}(\omega_s; \omega_1, \omega_s, -\omega_1)$ optical nonlinearity. Consequently, the nonlinear processes up to fifth-order can produce contributions to the optical frequency mixing, as well as those of cascade third-order processes. The laser-induced autoionizing tunable resonances are mostly preferable for a substantial enhancement of the optical frequency mixing efficiency and for other nonlinear conversion processes. The efficiency increasing at autoionizing resonances is substantial and the continuum structuring can be of practical interest. The induced resonance in the atomic continuum may be quite valuable on harmonic generation in UV and VUV range.

Important feature of the expected structure is the obtaining of an asymmetric profile, similar to that of Fano resonance, providing by quantum-mechanical interference between the two-photon 3s – 5s transition in sodium and the induced autoionizing state to the continuum structure. The efficient frequency mixing and observing of powerful signal wave requires a combination of phase-matching, larger focal spot to avoid breakdown, and longer Na cell length, which also contributes to the efficiency enhancement. Phase-matching can be accomplished in rare gases. Our measurements were made with phase-matched mixtures of Na vapor and xenon at a given density of Xe gas.

We can get more information about temporal and spatial line shape, if we use experimental technique with higher resolution in scanning the ionization spectrum. In order to obtain high
resolution in scanning the ionization enhancement in sodium, we use amplification stage for dye laser, which provides 50-mJ pulses. Besides, we apply linearly polarized radiation tunable around $\lambda_d = 602.3$ nm and $\lambda_d$ coincides with two-photon resonance $3s - 5s$ in Na. The dye lasers $\omega_d$, $\omega_d'$ and the coherent inducing $\omega_1$ beam, are focused by 20- and 30-cm focal length lenses, and overlap in the center of the heat pipe in a counterpropagating geometry. We should specially note, that in counterpropagating configuration – the output spectrum of the nonlinear optical mixing is free of Doppler broadening. Thus, further narrowing of the bandwidths of signal $\omega_s$ wave and of dye laser outputs is possible. The beams temporal nanosecond duration contribute to better resolution of the frequency scanning system, as well. The optimum tuning is provide by an optical delay between the interacting beams. Control of the polarized rotation of these beams, is also performed.

**Figure 7.** Ionization enhancement versus the laser tuning near the induced autoionizing resonance when scanning the signal linewidth $\Delta \nu_s$, cm$^{-1}$.

In Fig. 7, the ionization enhancement is plotted upon the laser tuning near the induced autoionizing resonance. The ionization signal is averaged over 100 laser pulses. The heat pipe produced a sodium density $\sim 2 \times 10^{14}$ atoms/cm$^3$. A sensitivity of about $10^{-2}$ in the measurement of the ionization enhancement was possible only by a careful optimization of experimental conditions, performed in order to minimize the background. The ionization enhancement is determined as a ratio of the ionization signal measured at induced autoionizing resonance, and this is compared with the ionization measured in the absence of inducing $\omega_1$ laser, i.e. when the continuum is not structured by fundamental $\omega_1$ beam. The line shape is asymmetric, following the spatial and temporal electromagnetic field distribution. The accuracy of this measurement provides clear evidence of an asymmetric line, which character of the line shape is typical - for the laser-induced autoionizing state in atomic systems. The cross section of photoionization of the two-photon $3s - 5s$ transition also increases, since we use in experiment powerful dye laser $I_d$, $I_d'$ intensities at a constant fundamental $I_1$ beam.
4. Discussion
In order to obtain the correct physical interpretation of the experimental results, we need to include the four-photon as well as six-photon processes of nonlinear frequency mixing – within the processes studied here. Such simultaneous action of several direct and cascade processes was well-known for the higher harmonic generation [11,12]. It turned out that these processes are quite important also for the laser-induced AI resonances. The direct six-photon process at AIS is determined by fifth order nonlinearity:

\[ I_s \sim |\chi^{(5)}(\omega_s; \omega_d, \omega_d', \omega_1, -\omega_1)|^2 N^2 I_d^2 I_1^2 I_d' \]

where \( N \) is the atomic density. Both consequent cascade four-photon processes are described by third order nonlinearities

\[ \chi^{(3)}(\omega_s; \omega_d', \omega_d, \omega_d') \]

and

\[ \chi^{(3)*}(\omega_s; \omega_1, \omega_s, -\omega_1) \].

The efficiency enhancement of the nonlinear process at induced AIS can be explained by the resonant increasing of the nonlinear optical susceptibility. As it is evident in Fig. 4, the saturation effect arises with the increasing of the intensities \( I_d, I_d' \). When \( \omega_d \) precisely corresponds to the two-photon transition \( 3s - 5s \), the saturation can be connected with a broadening of the resonant line after fundamental power decreasing, because of two-photon absorption. The enhancement of \( I_d' \) leads to a broadening of the induced autoionizing resonance and limits the output signal intensity \( I_s \). Another reason for saturation could be the dispersion of the excited atoms, when the processes of self-focusing and defocusing take place.

Depending on the duration of the pulses, the ionization may be complete in the central part of the focused region, and we can consider the parameters over the spatial distribution of the laser intensities. Recently, studies of induced autoionizing states include experimental results on nonlinear optical processes and photoionization in alkali, in alkaline–earth atoms etc. Experimental investigations are very useful in clarifying the role of the induced autoionizing resonances in nonlinear interactions of atoms when applying laser radiation \( \omega_1 \) field.

It is important to perform the experimental study both in the strong- and weak-field regime when referring to the fundamental \( \omega_1 \) intensity coupled the bound state to the continuum. At the increasing intensity, the width of the structure becomes dependent on the photoionization rate from the excited state. As a result, the line shape becomes dependent on the temporal and spatial intensity distribution of the fundamental \( \omega_1 \) beam. The main purpose of the study near the induced autoionizing nonlinear resonance is an interpretation of the line shape, taking into account the laser bandwidths and the hyperfine structure of atomic levels. The results provide a complementary information to that given by photoionization experiments. Besides, measurements performed at different vapor densities show a clear evidence of line-broadening effects.

Considering the accurate determination of the atomic parameters, the process of structuring the continuum in the conditions of experiment is found to be quantitatively consistent with the theoretical predictions. A careful optimization of the interaction conditions and of the sensitivity of the apparatus allow a measurement of dispersive profile of the autoionizing-like resonance suitable to an interpretation. According to the results, the signal \( \omega_s \) wave of the frequency mixing can be enhanced by introducing the laser \( \omega_1 \) beam and structuring the continuum.
The obtained results here involve a detailed study of the ionization process. In addition, experiments are carried out to control the ionization rate and at the same time – the efficiency of the optical frequency mixing. The $\omega_1$ radiation is used to couple an autoionizing state to the continuum at the required position to affect the induced nonlinear resonance. The ionization rate is found to be dependent on the frequency $\omega_1$. Results of detailed study of this process include also its effect on the efficiency of the frequency-mixing process.

5. Conclusion
The main obtained result in this experiment is an optimization of optical frequency mixing at phase-matching and using two-photon transition near autoionizing-like resonance. These processes can be applied for creating of high efficient conversion into UV and VUV range. It is also interesting to study the processes via induced Al states at various temporal delays between the pulses of intensities $I_d$, $I_e$, $I_1$. Using tunable laser beams, we can induce narrow nonlinear resonances in an arbitrary field of continuum, which realize both the ionization and the effective nonlinear frequency conversion. The induced autoionizing resonances have much advantages in order to optimize laser isotope separation (LIS) and the higher order harmonics generation into VUV and soft X-ray region.

6. References
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