Quantum Electronics **47** (11) 1005–1008 (2017)

NONLINEAR OPTICAL PHENOMENA https://doi.org/10.1070/QEL16488

Evolution of the Rayleigh scattering from mixed Ar/Kr clusters during their saturation with krypton atoms

I.A. Zhvaniya, M.S. Dzhidzhoev, A.V. Balakin, N.A. Kuzechkin, A.P. Shkurinov, V.M. Gordienko

Abstract. **The evolution of the Rayleigh scattering signal from mixed Ar/Kr clusters with variation in the partial Kr concentration in the initial gas mixture is investigated. An addition of krypton in small amounts to argon is found to cause an anomalously rapid increase in the Rayleigh scattering signal amplitude, which is due to a sharp increase in the size of clusters as a result of their saturation with krypton atoms. At a partial krypton concentration above 25 % in the initial mixture, the scattering signal amplitude is stabilised because of the condensation saturation during the cluster formation.**

Keywords: *Rayleigh scattering, mixed clusters, Ar, Kr, nanoplasma, X-rays.*

1. Introduction

Currently, the interest of researchers in mixed (i.e., consisting of different atoms or molecules) nanoclusters is constantly increasing [1]. Physical and chemical properties of clusters depend strongly on their structure and size. Mixed clusters are more promising and interesting objects than homogeneous ones from the point of view of controlling cluster parameters, because they provide an additional possibility for varying the composition, concentration, and segregation components. This circumstance explains the wide range of experimental studies of their structure [2, 3], which are maintained by simulation of the formation of mixed clusters of different compositions and sizes (see, e.g., [4, 5]). There are some fundamental problems, related to the excitation of mixed clusters by electromagnetic radiation: interatomic electron relaxation [6], fragmentation under IR and UV laser irradiation [7], generation of nanoplasma by high-intensity laser beams, etc. In addition, these structures are interesting from the applied point of view, for example, for generating X-ray and neutron beams [8] and for atmospheric chemistry studies [9].

Mixed clusters are conventionally obtained using the technique based on supersonic gas expansion through a nozzle into vacuum. The formation of these clusters has a number of specific features, which have been studied much less thoroughly than the details of the formation of noble-gas homogeneous clusters. The general tendency in the formation of mixed clusters is as follows: first, nanoparticles are formed from a heavier element with a higher binding energy under appropriate conditions. These particles become clusterisation centres for a lighter gas. As a result, segregation (i.e., separation of components) occurs to some extent in mixed clusters [10]. In addition, mixed clusters are formed in some narrow concentration range of mixtures used [11, 12].

The experimental methods that are used to reveal the presence of mixed clusters and determine their composition and structure include such complex methods as photoelectron X-ray spectroscopy [3, 10] and electron diffraction [12, 13]. Generally, diagnostics of mixed clusters is performed using a cooled gas mixture under a pressure up to 5 atm. At the same time, in the problems related to the interaction of high-intensity femtosecond laser radiation with clusters, to obtain a high energy absorption efficiency, it is necessary to form large clusters, consisting of 10^6 particles or even more. To this end, one must use gas mixtures under high pressure (above 20 atm) [14]. In this context, the search for simple methods of diagnostics of large mixed clusters and establishment of their formation conditions is an urgent problem.

In [15], we showed for the first time by an example of a Freon–argon gas mixture under a high pressure (about 25 atm) that mixed clusters can be diagnosed by analysing the spectrum of X-rays generated by these clusters exposed to femtosecond laser radiation of subrelativistic intensity. Caracteristic X-ray K-lines of both components forming a mixed cluster (chlorine and argon) indicate the presence of mixed clusters. Recently we have analysed the domain of existence of mixed Ar/Kr clusters [16]. Here, a question of applicability of the simple diagnostics of the existence of mixed clusters based on Rayleigh scattering data arises. One might expect that, in the case of binary mixtures containing components with significantly different scattering cross sections, an increase in the Rayleigh signal should indicate the occurrence of a component with a larger scattering cross section in the cluster. The argon–krypton mixture belongs to the mixtures

I.A. Zhvaniya, M.S. Dzhidzhoev, A.V. Balakin, A.P. Shkurinov, V.M. Gordienko Faculty of Physics, M.V. Lomonosov Moscow State University, Vorob'evy Gory, 119991 Moscow, Russia; International Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy Gory, 119991 Moscow, Russia; e-mail: zhvania@mail.ru, djidjoevms@mail.ru;
N.A. Kuzechkin Institute on Laser and Information Technologies, Russian Academy of Sciences, ul. Svyatoozerskaya 1, 140700 Shatura, Moscow region, Russia;
e-mail: lents125@mail.ru

Received 31 July 2017
Kvantovaya Elektronika **47** (11) 1005–1008 (2017)
Translated by Yu.P. Sin'kov

that satisfy this condition and are promising for the formation of mixed clusters.

In this paper, we report the results of studying the evolutionary features of the Rayleigh scattering from mixed Ar/Kr clusters formed as a result of gas-dynamic expansion of an Ar–Kr mixture located near a nozzle at room temperature under a pressure of 25 atm, with a varied partial krypton concentration in the initial gas mixture.

2. Experimental

Clusters were formed during adiabatic expansion of gas (or a binary gas mixture) emerging through a conical nozzle into vacuum. The diameters of the critical and output nozzle cross sections were 0.75 and 4 mm, respectively, and the half-angle at the cone vertex was 5°. More details concerning the parameters of the cluster beam generator can be found in [17]. A Rayleigh scattering signal was detected using a photoelectron multiplier, which was oriented normally to the propagation direction of the 445-nm probe radiation of a linearly polarised diode laser with a power of about 10 mW.

The Rayleigh scattering intensity I_R from a single cluster depends quadratically on the polarisability β of scattering centres and the number of atoms per cluster, N: $I_R = N^2 C\beta^2 I_0$, where C is a constant and I_0 is the incident radiation intensity [18]. The quadratic dependence on N is due to the fact that the cluster size is much smaller than the laser wavelength, due to which the atoms or molecules forming a cluster scatter radiation in phase. The total power of scattered radiation is n times higher (n is the number of clusters per unit volume); it is determined by the quantity nN^2. This yields the well-known cubic dependence of scattered signal on the gas pressure. The polarisability of krypton atoms exceeds that of argon atoms by a factor of about 1.5; therefore, the scattering cross section in the case of krypton increases by a factor of about 2.3 [19]. To study the specific features of a Rayleigh scattering signal, which can be caused by the formation of mixed clusters, we measured the dependence of the Rayleigh signal amplitude on the krypton concentration C_K in the initial Ar–Kr binary mixture and performed comparative methodical experiments aimed at recording a scattering signal from the clusters formed by pure krypton (Fig. 1). In the absence of krypton ($C_{Kr} = 0$), the Rayleigh signal amplitude from argon clusters is small, whereas for pure krypton ($C_{Kr} = 100\%$) it increases by about an order of magnitude. This difference in amplitudes was revealed in [14]; it is related to the difference in the scattering cross sections and sizes of argon and krypton clusters.

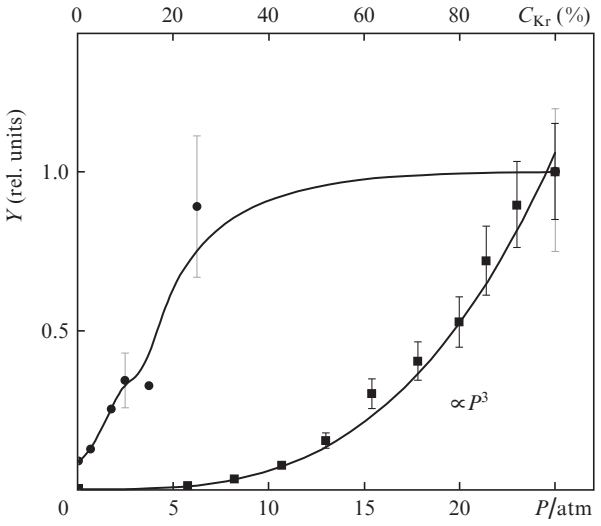

Figure 1. Dependences of the amplitude Y of the Rayleigh scattering signal from the clusters formed as a result of the expansion of (■) pure krypton and (●) Ar–Kr binary gas mixture on the krypton pressure P in pure gas and on the krypton concentration C_{Kr} in the binary mixture.

The cluster size in two limiting cases (pure argon or pure krypton) under our experimental conditions can easily be estimated from the known Hagena empirical formulas [20]. The conditions for the clusterisation onset in gas jets, which depend on the gas pressure, temperature, and nozzle parameters, are determined by the dimensionless (Hagena) parameter Γ:

$$\Gamma = k\left(\frac{d}{\tan\alpha}\right)^{0.85}\frac{p_0}{T_0^{2.29}},$$

where k is an empirical constant, which depends on the gas type ($k = 2890$ for Kr and 1650 for Ar); d is the critical diameter of the nozzle cross section (in μm); α is the nozzle half-angle; p_0 is the pressure in the high-pressure chamber (in 10^{-3} atm); and T_0 is the gas temperature in the high-pressure chamber (in K). The number of particles q in large clusters ($\Gamma > 1000$) is determined by the Hagena parameter: $q = 100(\Gamma/1000)^{1.8}$ [18]. Under our experimental conditions, an argon cluster consists of 1.3×10^6 atoms, while a krypton cluster consists of 3.6×10^6 atoms. The number of atoms in mixed Ar/Kr clusters probably ranges between these limiting values.

We found the Rayleigh signal amplitude to sharply increase with an increase in C_{Kr} for a binary mixture in the range of low krypton concentrations ($C_{Kr} < 25\%$). However, this pattern is not observed at similar pressures of pure krypton (see Fig. 1). The scattering from krypton clusters is approximated by a cubic power-law function, which is in agreement with the results of previous studies (see, for example, [14]). A sharp increase in the signal as a result of adding a small amount of krypton to the mixture is indicative of an increase in the size and number of clusters due to their cooling by argon monomers with a corresponding decrease in the argon concentration in clusters, up to its complete replacement with krypton. All these factors should manifest themselves in the Rayleigh signal amplitude because of the larger scattering cross section of krypton and its higher weight concentration in clusters [21].

To make sure that mixed binary clusters are formed at low krypton concentrations in the mixture, we implemented the diagnostic technique proposed by us in [15]; it is based on recording X-rays generated in the cluster nanoplasma. The excitation of the K transition in krypton atoms and generation of X-rays in the range $E \approx 12.7$ keV occurred when a gas-cluster jet was exposed to Ti:sapphire laser pulses with energy up to 50 mJ and focal peak intensity of about 5×10^{17} W cm^{-2}. The presence of mixed clusters in the mixture at low krypton concentrations is confirmed by the X-ray spectrum of irradiated gas-cluster jet from a binary Ar–Kr mixture with $C_{Kr} = 10\%$ (Fig. 2a). This spectrum exhibits two characteristic lines, which are due to the K transitions in argon ($E \approx 3.1$ keV) and krypton ($E \approx 12.7$ keV) ions; this

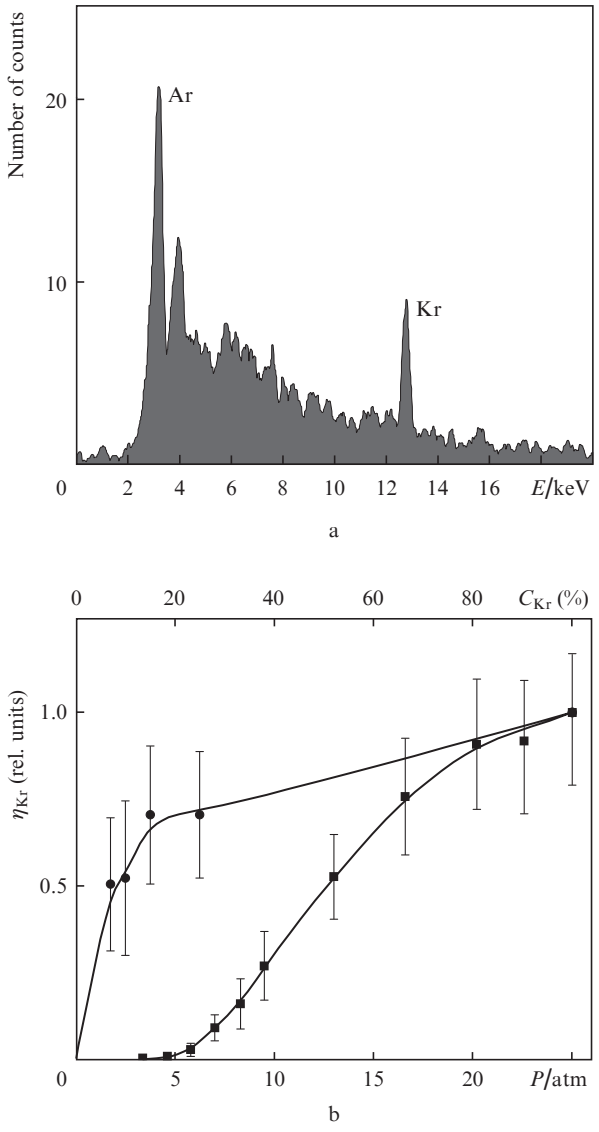

Figure 2. (a) X-ray spectrum of cluster nanoplasma formed as a result of laser irradiation of a gas-cluster jet produced by the expansion of a binary Ar–Kr mixture with a krypton concentration of 10% and (b) dependences of the generation efficiency η_{Kr} of X-ray krypton line in the spectra of (■) clusters formed by the expansion of pure krypton and (●) Ar–Kr binary gas mixture on the krypton pressure P in pure gas and on the krypton concentration C_{Kr} in the binary mixture.

pattern is associated with the existence of mixed clusters, containing both these components. In addition, there is a higher energy (about 4 keV) satellite near the argon line. Its occurrence was related in [22] to the excitation of exotic Rydberg states in helium-like argon ions; the $n^1P_1 \rightarrow 1^1S_0$ transitions correspond to these states at $n > 5$.

Our study revealed that the efficiency of laser energy conversion into the krypton X-ray line (the ratio of the energy in the line to the laser pulse energy) depends on the relative krypton concentration in the mixture (Fig. 2b) [16] in the same way as the Rayleigh scattering signal (see Fig. 1). At the same time, the X-ray output for homogeneous clusters increases much more slowly. This behaviour of the intensities of X-ray emission and Rayleigh scattering (both processes depend on the size and concentration of clusters) confirms the saturation of clusters with krypton, which manifests itself in the Rayleigh scattering signal.

3. Conclusions

Addition of a small amount of krypton to a clusterised argon gas at room temperature and a pressure of 25 atm was found to lead to an anomalously fast rise of the Rayleigh scattering signal, which is related to a sharp increase in the size of clusters saturated with krypton atoms. The scattering signal is stabilised when the partial krypton concentration in the initial mixture exceeds 25%, which is indicative of the saturation of condensation and stabilisation of the cluster formation.

The dependence of Rayleigh signal on the krypton concentration in the mixture was found to be similar to the dependence of the generation efficiency of X-ray krypton line, excited in a gas-cluster jet irradiated by femtosecond laser pulses with subrelativistic intensity of $\sim 5 \times 10^{17}$ W cm^{-2}; the reason is that both these processes are determined by the size and concentration of clusters. This observation confirms that mixed clusters are indeed saturated with krypton.

The proposed diagnostic technique for mixed clusters, which is based on analysing the Rayleigh scattering signal, can be used to detect clusterisation of heavy component in different binary cluster-forming mixtures of atomic/molecular gases.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant Nos 16-32-60171 and (in part) 17-02-01217 A).

References

1. Makarov G.N. *Usp. Fiz. Nauk*, **187**, 241 (2017).
2. Pokapanich W., Björneholm O., Öhrwall G., Tchaplyguine M. *Radiat. Phys. Chem.*, **135**, 45 (2017).
3. Nagasaka M., Serdaroglu E., Flesch R., Rühl E., Kosugi N. *J. Chem. Phys.*, **137**, 214305 (2012).
4. Winkler M., Harnes J., Børve K.J. *J. Phys. Chem. A*, **117**, 13127 (2013).
5. Marques J.M.C., Pereira F.B. *J. Comput. Chem.,* **34**, 505 (2013).
6. Fasshauer E., Foerstel M., Mucke M., Arion T., Hergenhahn U. *Chem. Phys.*, **482**, 226 (2017).
7. Apatin V.M., Lokhman V.N., Makarov G.N., Ogurok N.D., Petin A.N., Ryabov E.A. *J. Exp. Theor. Phys.*, **120**, 191 (2015).
8. Heidenreich A., Jortner J., Last I. *Proc. Natl. Acad. Sci.*, **103**, 10589 (2006).
9. Xu J., Finlayson-Pitts B.J., Gerber R.B. *J. Phys. Chem. A*, **121** (12), 2377 (2017).
10. Tchaplyguine M., Lundwall M., Gisselbrecht M., Öhrwall G., Feifel R., Sorensen S., Svensson S., Mårtensson N., Björneholm O. *Phys. Rev. A*, **69**, 31201 (2004).
11. Kim S.S., Stein G.D. *J. Appl. Phys.*, **51**, 6419 (1980).
12. Danylchenko O.G., Kovalenko S.I., Konotop O.P., Samovarov V.N. *Low Temp. Phys.*, **41**, 637 (2015).
13. Konotop O.P., Kovalenko S.I., Danylchenko O.G., Samovarov V.N. *J. Clust. Sci.*, **26**, 863 (2015).
14. Ditmire T., Donnelly T., Rubenchik A.M., Falcone R.W., Perry M.D. *Phys. Rev. A*, **53**, 3379 (1996).
15. Gordienko V.M., Dzhidzhoev M.S., Zhvaniya I.A., Trubnikov D.N., Fedorov D.O. *Laser Phys. Lett.*, **11**, 36003 (2014).
16. Zhvaniya I.A., Dzhidzhoev M.S., Gordienko V.M. *Laser Phys. Lett.*, **14**, 096001 (2017).

17. Gordienko V.M., Dzhidzhoev M.S., Zhvaniya I.A., Petukhov V.P., Platonenko V.T., Trubnikov D.N., Khomenko A.S. *Pis'ma Zh. Eksp. Teor. Fiz.*, **91**, 329 (2010).
18. Dorchies F., Blasco F., Caillaud T., Stevefelt J., Stenz C., Boldarev A., Gasilov V. *Phys. Rev. A*, **68**, 23201 (2003).
19. Rice E., Lee J. NASA-CR-190252, NAS 1.26190252 25 (1989).
20. Hagena O.F. *Rev. Sci. Instrum.*, **63**, 2374 (1992).
21. Zhang L. Chen L.-M., Yuan D.-W., Yan W.-C., Wang Z.-H., Liu C., Shen Z.-W., Faenov A., Pikuz T., Skobelev I., Gasilov V., Boldarev A., Mao J.-Y., Li Y.-T., Dong Q.-L., Lu X., Ma J.-L., Wang W.-M., Sheng Z.-M., Zhang J. *Opt. Express*, **19**, 25812 (2011).
22. Colgan J., Abdallah J., Faenov A.Y., Pikuz T.A., Skobelev I.Y., Fukuda Y., Hayashi Y., Pirozhkov A., Kawase K., Shimomura T., Kiriyama H., Kato Y., Bulanov S.V., Kando M. *High Energy Density Phys.*, **7**, 77 (2011).