Asymmetry of optical excitation of a copper atom resonance doublet

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The asymmetry of optical excitation of a copper atom resonance doublet in mixtures of copper vapor with inert gases has been investigated. The effect of laser excitation at λ = 327.4 nm resonant to the long-wave component of the doublet of a copper atom $4^2S_{1/2}$–$4^2P^0_{1/2}$ has been found to be accompanied by changes in populations of the both doublet sublevels, while the laser excitation at λ = 324.8 nm resonant to the another doublet component $4^2S_{1/2}$–$4^2P^0_{3/2}$, is accompanied by changes in population of only one sublevel. It is assumed that the effect is caused by the asymmetry of optical excitation functions of doublet components $4^2P^0_{1/2,3/2}$ in the presence of atom–atom collisions.

Introduction

Resonance doublets of elements of the first group are traditional objects of experimental and theoretical investigations in physics of excited states. For chemical elements having relatively higher vapor pressures, for example, alkali metals, considerable data on cross sections and rates of energy transfer between doublet sublevels are accumulated.[1,2] For alkali atoms, the appearance of satellites of resonance lines was experimentally discovered and studied,[3–5] and theories were developed for description of the central part and wings of profiles of resonance lines formed in the processes of atom–atom collisions.[6]

High-temperature ceramic cells[7,8] and tunable lasers[9] allow investigation of elements with a low vapor pressure. Consequently, the list of elements, with whose vapors the analogous study can be performed, can be extended significantly. The copper is one of the most interesting elements in the list of high-temperature elements of the first group.

First, resonance doublets of copper atoms are high working levels of high-efficiency gas-discharge lasers.[10–12] Some properties of these lasers, for example, partial competition of lasing lines in a copper laser, may be connected with the transfer of excitation energy between components of the resonance doublet $^2P^0{}_{1/2,3/2}$.

Second, copper is a d-element, and it is worth comparing the properties of resonance doublets of d-elements with analogous doublets of alkali elements. Finally, energy defects ΔE between components of the copper doublet are 30 times larger than those of sodium and two times smaller than those of cesium at the same order of the levels (the upper doublet component has a moment of 3/2, and the lower one has a moment of 1/2). This allows the efficiency of different gas-kinetic processes to be systematized with respect to the magnitude of $\Delta E/kT$.

This paper presents the results of observation of copper vapor fluorescence at optical excitation of components of the copper resonance doublet in an extended column of copper vapor. In contrast to the resonance doublet of alkali atoms, components of the copper resonance doublet have two channels of optical decay: to the ground state in the UV region at the lines mentioned above and to metastable states at three lines of the visible region, namely λ = 510.6 nm ($^2P^0_{3/2} - {}^2D_{5/2}$), λ = 570.0 nm ($^2P^0_{3/2} - {}^2D_{3/2}$), and λ = 578.2 nm ($^2P^0_{1/2} - {}^2D_{3/2}$). This fact allows us to analyze the density behavior of resonance states by fluorescence signals in both the UV and visible regions. The presence of the channel in the visible region allows the excitation and fluorescence channels to be spectrally separated, observations to be carried out along the direction of propagation of the exciting radiation, and investigations to be conducted at low vapor densities.

Experimental

The schematic view of the experiment is shown in Fig. 1. The copper vapor was generated by thermal evaporation of the metal copper in a cylindrical BeO ceramic cell, placed coaxially in a quartz vacuum-tight housing with optical windows at the ends.

A tungsten heater on the outer surface of the ceramic tube was thermally insulated by a system of thermal screens made as three thin-wall cylinders of molybdenum foil arranged coaxially with the ceramic tube and the external quartz housing. The cylinder diameters were 24, 42, and 54 cm, respectively. The length of each cylinder was 40 cm, which is 3.5 cm longer than the length of the ceramic tube. This design allowed us to create an 18-cm long zone of homogeneous heating in the central part of the cell. A disadvantage of this design is a high energy consumption caused by high losses for emission. A platinum-rhodium thermocouple was set directly in the cell.

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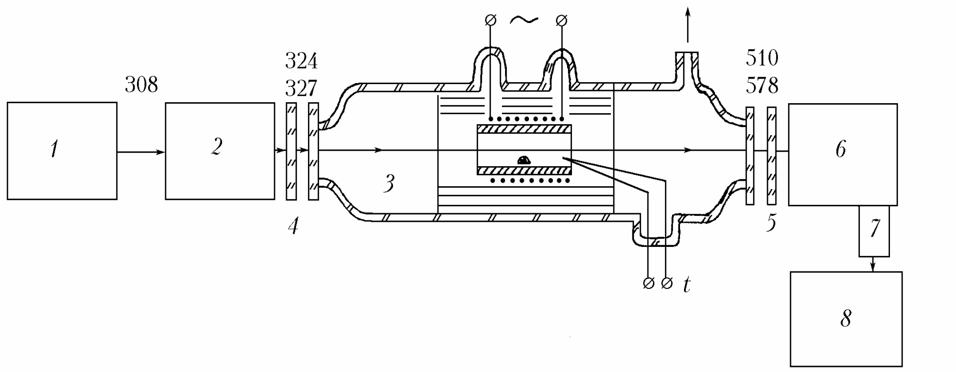

Fig. 1. Block diagram of the experiment: excimer laser *1*, dye laser with frequency doubling *2*, cell *3*, UV filter *4*, visible filters *5*, monochromator *6*, photodetector *7*, and Brookdeal system for detection of signals *8*.

In high-temperature cells of this design, a vacuum-tight housing is filled with some inert gas to prevent vapor from deposition on windows and walls. The density of the buffer gas should be higher than the vapor density and usually higher than 1–10 Torr. The minimal vapor density is determined by the level of optical noise generated by the laser-induced fluorescence of cell elements, in particular, by the fluorescence of windows, and by thermal radiation of the tungsten heater, at which the fluorescence signal of the copper vapor is still recorded reliably.

For optical excitation of the vapor at the copper resonance lines $\lambda = 327.4$ or 324.8 nm, we used a dye laser with the frequency doubling. An Oxazine-17 dye laser was excited by the excimer $XeCl^*$ laser. The frequency was doubled in the KDP crystal. The converted UV radiation had a linear polarization. The pulsed energy of the UV radiation was 100–200 μJ at a full length of the laser pulse of 6 ns.

Taking into account all the above-said, the system for recording of fluorescence signals included a MDR-23 monochromator, a FEU-100 photomultiplier, and a Brookdeal analog system for separation of signals from the noise. This recording system performed the operations of gating, integration, and accumulation of signals. The analog fluorescence signal was recorded at a copper vapor density N_{Cu}, being higher than 10^9 cm^{-3}.

Results

Figure 2*a* shows three spectral transitions of the visible region ($\lambda = 510.6$, 570.0, and 578.2 nm) observed in the fluorescence spectrum at the exitation of the copper vapor in a mixture with light buffer gases by radiation of a laser tuned at the long-wave component of the doublet ($\lambda = 327.4$ nm).

It is seen from Fig. 2 that this fluorescence spectrum corresponds to excitation of not only the lower, but also the upper sublevels of the resonance doublet.

Observation of radiation from not only the lower, but also the upper sublevel of the resonance doublet provided optical excitation of only the lower sublevel principally corresponds to the idea that under these conditions the energy is transferred between the doublet components in atom-atom collisions with either vapor particles or particles of a buffer gas. These collisions should satisfy the condition $\tau_{col} < \tau_{rad}$, where τ_{col} and τ_{rad} are the collision time and the time of the radiative decay of excited states, respectively. In the limit, at collisional mixing the populations of copper doublet components should tend to the ratio of statistical weights, that is, to two (the Boltzmann factor is close to unity).

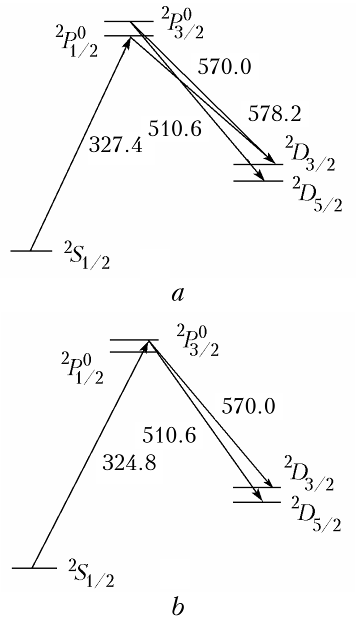

Fig. 2. Optical transitions in the Cu atom observed at optical excitation of the mixture of copper vapor and inert gases at λ = 327.4 (*a*) and 324.8 nm (*b*).

According to the principle of detailed equilibrium, at transfer of the excitation between doublet components in atom-atom collisions, when the excitation wavelength changes from 327.4 to 324.8 nm, that is, at optical excitation of the upper sublevel, the spectral composition of fluorescence should be unchanged, although the intensity ratio of the lines may be different. However, as the laser was tuned to $\lambda = 324.8$ nm, observations of the spectral composition of vapor fluorescence showed that the condition of detailed equilibrium for the copper multiplet failed. From Fig. 2*b*, which shows the diagram of the fluorescence spectrum of copper vapor at optical excitation of the upper sublevel of the multiplet, one can see that the spectrum contains only one component, namely, the line $\lambda = 510.6$ nm and, consequently, the lower component of the doublet is not excited.

Thus, it is found that there are conditions of vapor excitation, under which the radiation of the long-wave component of the resonance doublet at $\lambda = 327.4$ nm populates both sublevels of the resonance state, while the short-wave component at $\lambda = 324.8$ nm populates only one sublevel. This effect was called the asymmetry of optical excitation of a resonance doublet. The presence of a flow of population from the lower component of the doublet $^2P^0_{1/2}$ to the upper component $^2P^0_{3/2}$ and its absence in the inverse direction allow us to draw an analogy with the *p–n* transition in radioelectronics. In this meaning, the copper doublet can be considered as some optical analog of a diode, "conducting" population only in one direction due to the asymmetry of atomic collisions.

It is interesting to find the boundaries of physical conditions, under which the asymmetry of the optical excitation is considered. As a measure of asymmetry, we took the ratio of intensities of green and yellow lines $\eta = J_{510.6}/J_{578.2}$ at excitation of the lower component of the doublet by radiation at $\lambda = 327.4$ nm. Figure 3 shows the dependence of η on the vapor excitation conditions. In the experiments, we varied the concentrations of copper and buffer gases (Ar, Ne, He). Therefore, to make the figure more illustrative, we show variations of the buffer gas density in units of pressure (torrs).

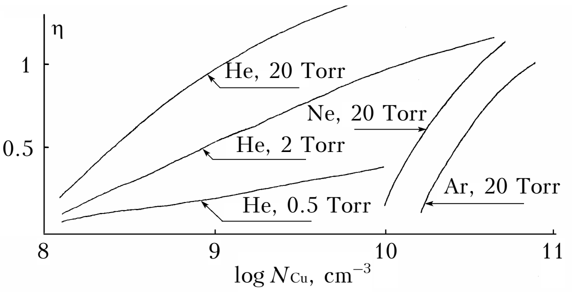

Fig. 3. Dependence of the measure of asymmetry η on observation conditions.

It has been found that at excitation by radiation at $\lambda = 327.4$ nm the value of η depends both on the kind and the pressure of the buffer gas and on the density of Cu vapor. As is seen from Fig. 3, the asymmetry is observed at extremely low densities of the metal vapor $N_{Cu} \sim 10^9$ cm^{-3} and rather low densities of buffer gases. The maximal asymmetry corresponds to mixtures of metal vapors with He, and the effect starts to show itself at He densities higher than 10^{-1} Torr. For mixtures of metal vapors with Ne and Ar, a significant asymmetry is observed both at high vapor densities ($N_{Cu} > 10^{11}$ cm^{-3}) and at significantly high densities of inert gases.

Experiments with mixtures of the Cu vapor with heavy inert gases Xe and Kr have shown that quenching of fluorescence is observed in these mixtures at vapor excitation by radiation at wavelengths of 324.8 and 327.4 nm. Estimates show that the cross sections of quenching by these gases are high: $\sigma \sim 10^{-15}$ cm^2.

Tuning of the dye laser radiation near the line $\lambda = 327.4$ nm shows that under condition of observation of asymmetry the intensities of yellow and green lines are maximal near the exact resonance of the laser radiation with the copper line.

At the copper vapor concentration N_{Cu} higher than 10^{15} cm^{-3}, the optical excitation of the resonance doublet gave rise to superluminescence at the visible-region lines $\lambda = 510.6$ and 578.2 nm. The asymmetry of excitation holds in this case.

Discussion

We studied the asymmetry of excitation at significantly lower concentrations of the copper vapor N_{Cu} and an order of magnitude lower pump intensities I_p than those used in Ref. 13. This choice of conditions is not arbitrary.

At high values of N_{Cu} and I_p, the radiation from the levels $^2P^0_{1/2}$ and $^2P^0_{3/2}$ becomes stimulated. Due to saturation, the population of each excited level becomes comparable with that of the ground state $^2S_{1/2}$. The stimulated character of emission at the studied lines of a copper atom and the considerable population do not allow us to categorically relate the intensity ratio of the lines to only collisional mixing. Thus, at a high pressure of the buffer gas, when there is a strong collisional relation between levels, the difference in the intensity of the studied lines may result from competition between them. This competition is caused by the different rate of development of the stimulated emission at the yellow and green lasing lines at different pressures of the buffer gas.

The significant redistribution of population between components of the copper doublet at high values of the pump intensity and high concentrations of the copper vapor may be caused by the following processes: Stokes $^2P^0_{1/2} \to {}^2P^0_{3/2}$ or anti-Stokes $^2P^0_{3/2} \to {}^2P^0_{1/2}$ of the stimulated Raman scattering at electronic transitions (SERS).

The SERS processes can be pumped not only by the UV radiation of the second pump harmonics, but also by the stimulated radiation of the yellow and green copper lines.

The necessity to perform this study at the minimal possible intensity of the pumping radiation and low concentrations of copper atoms is dictated not only by the high probability of SERS processes, but also by the square intensity dependence of other possible two-photon parasitic processes, leading to the population redistribution in the sublevels $^2P^0_{1/2}$ and $^2P^0_{3/2}$.

The results obtained in the study of optical pumping of potassium[14] and sodium[15] vapor also say for this necessity. It was found that at optical pumping (at the D_2 line) of the upper level of the potassium doublet $4^2P^0_{3/2}$ in the presence of helium, the stimulated resonance emission from the lower level $4^2P^0_{1/2}$ (D_1 line) is observed. The conditions for observation of emission at the long-wave component of the doublet D_1 are high concentrations of the potassium vapor and the buffer gas (helium) along with the high pump intensity. This means that under these conditions the some stimulated radiation at D_1 is induced in the medium in addition to the pumping radiation at D_2, and this additional radiation can populate optically the lower level of the doublet (at least, before and after the waist region, free of the population inversion). In opinion of the authors of Ref. 14, due to the difference in statistical weights, the pumping of the lower level of potassium did not led to emission from the upper level.

It is logically to suppose that at the above-mentioned similarity between structures of atomic levels of alkali metals and copper the analogous processes can take place in copper as well. Thus, the increase of the helium pressure at high-intensity pumping of the copper doublet upper level, by analogy with Ref. 14, can give rise to emission at the long-wave resonance copper line. As a result, the both resonance frequencies act simultaneously on the copper vapor.

There are two ways to overcome this mistake in interpretation of results of copper vapor optical pumping. It is the direct observation of the radiation intensity in both visible and infrared channels of optical decay of the $^2P^0_{1/2}$ and $^2P^0_{3/2}$ copper atomic levels or the experiment at a low pump power and a low concentration of the copper vapor, being much lower than the threshold values for emission at the long-wave resonance line. Just these experimental conditions allow us to eliminate the influence on the results of the processes mentioned above, such as competition, SERS, and other parasitic processes,. Therefore, we performed the study at the values of $N_{\rm Cu}$ and $I_{\rm p}$, at which stimulated transitions are absent and the emission at the studied copper atomic transitions has a spontaneous character. This approach has allowed us to study systematically the asymmetry of excitation of the copper atomic doublet using He, Ne, Ar, Kr, and Xe as buffer and mixing gases.

Unfortunately, due to a high noise level in the UV region, we failed to determine how the collisional population redistribution between components $^2P^0_{1/2}$ and $^2P^0_{3/2}$ of the resonance doublet affects the intensity of the copper atomic resonance lines $^2P^0_{1/2} \to {}^2S_{1/2}$ (λ = 327.4 nm) and $^2P^0_{3/2} \to {}^2S_{1/2}$ (λ = 324.8 nm), competing with the yellow and green lines. As it was already mentioned in Introduction, these lines have common upper levels $^2P^0_{1/2}$ and $^2P^0_{3/2}$.

To understand the observed phenomenon of asymmetry in excitation of components of the copper resonance doublet, it is necessary to assume that the doublet components have optical excitation functions, significantly asymmetric relative to the exact resonance. Figure 4 shows conditionally the form of these asymmetric functions, distinguishing from the typical ones by the presence of a wide red satellite.

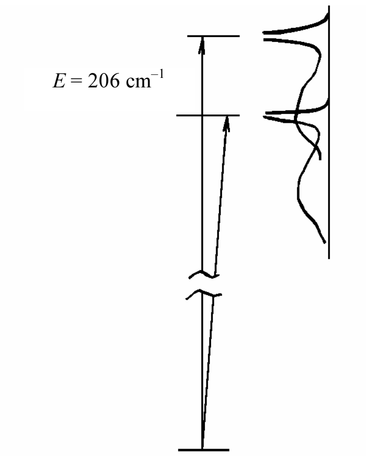

Fig. 4. Components of the copper resonance doublet and conditional form of their excitation function.

In this case, the laser radiation, tuned at the lower spectral component of the doublet (λ = 327.4 nm), is absorbed not only by this component, but also by the red satellite of the upper component of the doublet, and when the laser is tuned at the short-wave spectral component (λ = 324.8 nm), its radiation “passes by” the blue wing of the lower component.

Within the framework of the hypothesis formulated above, the maximal intensity of radiation at a wavelength λ = 510.6 nm at a high pressure of the buffer gas corresponds not to the satellite maximum of the resonance doublet short-wave component, but to the exact tuning of the laser radiation at the resonance line λ = 327.4 nm. As in the case of excitation of the potassium vapor,[14] this maximum is caused by the fact that at the exact resonance of the pumping radiation with the spectral component of the doublet λ = 327.4 nm the lifetime of the photon, scattered in the medium, (and the optical path length) increases due to the resonance radiation reabsorption. The increase of the photon optical path length increases the probability of the radiation absorption at λ = 327.4 nm by the satellite of the doublet upper component.

Conclusion

It should be noted that now we know a number of optical effects observed upon the propagation of resonance or quasiresonance radiation in a metal vapor. In particular, as the quasiresonance radiation propagates in a metal vapor, the following effects are observed: the fluorescence and superluminescence at optical transitions adjacent to the resonance ones and at some atomic transitions, having no optical bond with the ground and resonance levels, as well as even at optical transitions in ions. Such transitions were observed in spectra of Ba atoms and ions upon the propagation of excimer laser radiation through the mixture of Ba vapor with light inert gases.[16] Note that these effects are observed at a negative (toward the red side) detuning of the pump radiation from the exact resonance with atomic transitions. An interesting case of optical excitation of the resonance multiplet in the sodium vapor[17] was observed, when the frequency of high-power laser radiation was tuned in the spectral range, lying higher than the upper component of the doublet. In the presence of helium, the both components of the multiplet were excited.

Then, it is known that if the pump radiation is detuned from the exact resonance with the resonance state of an atom in an atomic medium, having intermediate excited states (in copper, for example, these are the metastable states $^2D_{3/2}$ and $^2D_{5/2}$), high-efficient SERS referred to as electronic can take place.[16] The investigations performed in Ref. 18 have shown that as the quasiresonance radiation propagates in the Cu vapor, SERS takes place at the scattering at transitions ($^2S_{1/2} - {}^2D_{3/2,5/2}$). In this case, SERS is observed at the detuning of the pump radiation to the red region from the exact resonance, although by the matching condition the detuning to the blue region is optimal. By analogy, this effect can be called the asymmetry of SERS excitation.

When analyzing results of optical pumping, the cases that emission proceeds from levels lying higher than the excited levels (for example, in aluminum[19] and other elements[20]) are often noted. It is quite probable that some of these cases have the same nature as the asymmetry observed in the copper.

The above-proposed mechanism of asymmetry should be considered as a working hypothesis, and it obviously calls for further investigations. In particular, taking into account that the asymmetry was studied at pumping by only linearly polarized UV radiation, it is interesting to study the asymmetry at other types of polarization of the pumping radiation. From the viewpoint of refining the mechanism of formation of the asymmetry, it is of interest to study the behavior of radiation in the UV channel of optical decay of the $^2P^0_{1/2}$ and $^2P^0_{3/2}$ levels of a copper atom at variable pressures of the copper vapor and inert gases.

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