Research Article Vol. 40, No. 1 / January 2023 / Journal of the Optical Society of America B 151

Journal of the Optical Society of America B

OPTICAL PHYSICS

Effect of absorption oscillation of resonant radiation observed in a compact installation for hyper-polarization of ^{129}Xe

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Received 8 September 2022; revised 19 November 2022; accepted 3 December 2022; posted 5 December 2022; published 20 December 2022

This work presents the discovery and study of a new, to the best of our knowledge, effect of oscillation of resonant radiation absorption in optical cells with rubidium vapor in the presence of xenon and nitrogen inside an installation for xenon polarization by spin-exchange optical pumping. This effect was observed at temperatures of 100°C–130°C, partial xenon pressure exceeding 100 kPa, total gas mix pressure of 400 kPa, and power of broadband ($\Delta\lambda = \sim 2$ nm) laser radiation over 2 W. The highest registered magnitude of power oscillations of the transmitted radiation exceeded 20%, the oscillation period depending on the temperature and lying in the range of 4.8–7 s. The conducted measurements of the parameters of the transmitted radiation lead to the conclusion that the discovered effect is related to concentration oscillations of the atomic rubidium vapor, which probably arises due to cyclic dimerization of rubidium or an oscillating continuous chemical reaction of rubidium and the optical cell contents.

https://doi.org/10.1364/JOSAB.475164

1. INTRODUCTION

The effects observed as the atomic rubidium vapors interact with optical radiation in an optical cell have a multitude of scientific and technological applications: atomic clocks, magnetometers, gyroscopes [1,2], UV radiation sources [3], and generation and detection of THz radiation [4,5]. One of emerging applications of rubidium is hyperpolarization of noble gases (xenon, helium) by spin-exchange optical pumping (SEOP) for further use in magnetic resonance tomography and nuclear magnetic resonance spectroscopy [6]. The SEOP method consists in polarization of the nuclei of xenon-129, -131, or helium-3 arising from collisions with rubidium atoms, whose electronic spins have been polarized by optical radiation. Advancements in this field are in many respects due to the promise of clinical applications of hyperpolarized (HP) xenon that led to development of commercial systems for HP xenon production at rates of ~1 liter/h [7–10]. Those systems employ comparatively large optical cells with volumes of about one liter heated to 70°C–90°C for optimal concentration of rubidium vapor containing a gas mixture under pressures of up to 2 atm [11,12].

At the same time, there exists an enormous class of problems related to applied NMR spectroscopy, which does not require large volumes of polarized gas to perform a single measurement, and in which several cm^3 of gas would be sufficient to fill the spectrometer cell. Hence, there arises an important problem of development of a compact device with a small-volume optical cell, able to produce modest quantities of polarized gas sufficient for several measurements. When using small cells, it is possible to adjust the SEOP parameters in wider ranges, in particular, raising the maximal working pressure and temperature of the cell. In the process of development of such a device, we came upon an effect of periodic modulation of the intensity of the transmitted resonant radiation with large (> 20%) magnitude and period (~5 s), which could be observed within a narrow range of temperatures subject to a number of conditions. In connection to the developed device, this effect is rather detrimental because it may be already quite hard to achieve high SEOP efficiency even under stationary conditions. Therefore, the main goal of the present study was to identify the parameters of the polarization process, which do not give rise to this effect. Nevertheless, because we have not found any references to the discovered effect in published research and, as we foresee, it may be of interest to other researchers, we offer the results of our studies in this work and advance a possible explanation of the nature of this phenomenon.

2. EXPERIMENTAL SETUP

The identified effect was discovered when researching SEOP processes of xenon in rubidium vapors taking place in a prototype of a table-top xenon polarizer whose optical layout is shown in Fig. 1. The output of a diode laser delivering 4 W within a

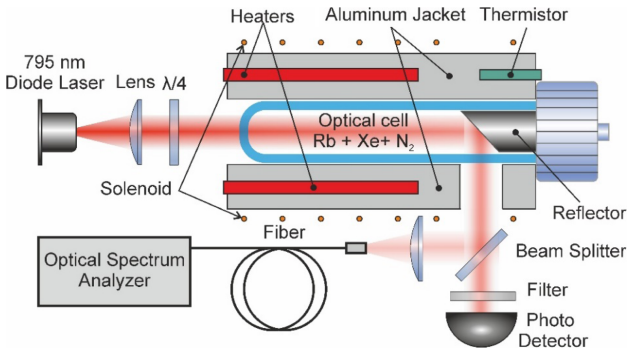

Fig. 1. Schematic diagram of the experimental prototype of a table-top xenon hyperpolarizer.

~2 nm spectral line was collimated through a lens and further guided into a thick-walled optical cell with the internal volume of 10 ml containing 100 mg of metallic rubidium. In the distal end of the cell, a metal reflector was installed that directed the radiation passing through the rubidium vapor onto a photo-detector and an optical spectrum analyzer. The internal diameter of the cell made of borosilicate glass was 15 mm and the optical path length from the proximal end of the cell to the reflector was approximately 85 mm. The laser beam diameter matched that of the cell, but because of inhomogeneity of the diode laser output, the beam area did not exceed 50% of the cross-section area of the cell cavity. The cell was placed inside an aluminum sheath heated by two electric AC-powered heaters with total power of 250 W. The current temperature was measured with a thermistor installed into the sheath. The reflector was made of a titanium alloy, and the cell was sealed with a fluoroplastic plug, into which a needle valve was built. More detailed description of the cell design is in the work [13]. The cell was filled using a vacuum station with the residual pressure of 0.01 Torr and gases in balloons with purity of 99.9994%. Apart from rubidium and xenon, also nitrogen was added into the cell to suppress spontaneous radiation generated by relaxation of rubidium that destroys its polarization [14]. Prior to filling the cells with the working gas mix, we conducted three cycles of pumping each cell down to the residual pressure and subsequent filling it with nitrogen to the pressure of 2 atm.

Because SEOP requires circularly polarized radiation and magnetic field parallel to the optical axis, a quarter-wave plate was inserted into the beam before the cell and a magnetic coil was wound around the aluminum sheath, which, when powered, created magnetic field with the strength of about ~2 mT. Because the magnetic field induced by the coil is much stronger than the background Earth field (50 μT), the condition for optical pumping can be created without an additional magnetic shield.

3. RESULTS

The standard procedure of xenon polarization is conducted as follows. The prepared cell is installed into the aluminum sheath, the laser beam is turned on and the radiation power transmitted through the cold cell is measured. After that, the heater is turned on. As the cell's temperature rises, the higher rubidium vapor concentration leads to reduction of the transmitted radiation power. After the cell has reached the working temperature, the transmitted power is measured again, and magnetic field is turned on, which creates the conditions for optical pumping of rubidium atoms, that is for polarization of their electron spins. In this process, the optical medium is bleached, and the power of radiation passing through the cell rises once more. Registering the transmitted radiation power and taking into consideration the previous measurements, it is possible to estimate the rubidium polarization degree, which determines the highest possible polarization of xenon nuclei.

In all the foregoing, it is expected that the power of the transmitted radiation in all the three measurements will remain constant (assuming constant temperature of the cell). Nevertheless, in the course of activities on optimization of the gas mix and working temperature of the cell it was found out that certain conditions give rise to large oscillations of the transmitted radiation power both in the presence and absence of the magnetic field, whereas the radiation parameters (power, polarization, spectrum) at the entrance to the cell remain highly stable, as does the cell temperature. The potentially thinkable effect of heaters and magnetic fields created by them may be safely discarded because the mentioned oscillations were equally observed with the heaters powered off during the passive cooling process.

Figure 2 presents a typical time-trace of the transmitted radiation power in the process of cell heating with a gas mix leading to oscillations (partial pressures of ^{129}Xe was 150 kPa, that of N_2, 250 kPa).

The graphic plot indicates that as the cell temperature rises, the transmitted radiation power drops off, but when temperature crosses 101°C, the radiation power begins to oscillate with ever higher amplitude, whereas the oscillation period becomes shorter [Figs. 2(b) and 2(c)], whereas dependence of the period on temperature is close to linear [Fig. 3(a)]. After reaching the optimal temperature of 117°C–120°C, the oscillation amplitude diminishes with both maximal and minimal power levels dropping at the same time [Fig. 3(a)]. At the cell temperature exceeding 127°C, oscillations die out altogether.

Our observations demonstrate that under conditions of constant temperature within the range of 101°C–127°C, oscillations with stable period and amplitude may continue at least for several hours without any tendency to attenuation.

During the observed oscillations, radiation spectra at highest, middle, and lowest transmittance were recorded [time points P1, P2, and P3 in Fig. 2(c)], the results are given in Fig. 3(a).

The graph shows that the variation of the transmitted radiation power is related to the variation of absorption at the resonant rubidium line. This dependence, in our opinion, is a clear indication that the observed effect stems from the processes taking place within the cell and cannot be explained by purely technical causes.

Further, during our studies a number of observations were made that, as we are inclined to believe, suggest the photo-induced nature of the discovered effect. After the temperature was raised up to 131°C–132°C, at which point no oscillations could be registered, it turned out possible to excite transient damped oscillations by momentarily shutting off the laser beam [Fig. 4(a)]. In this case, the initial oscillation amplitude depends upon the duration of beam blocking. The highest

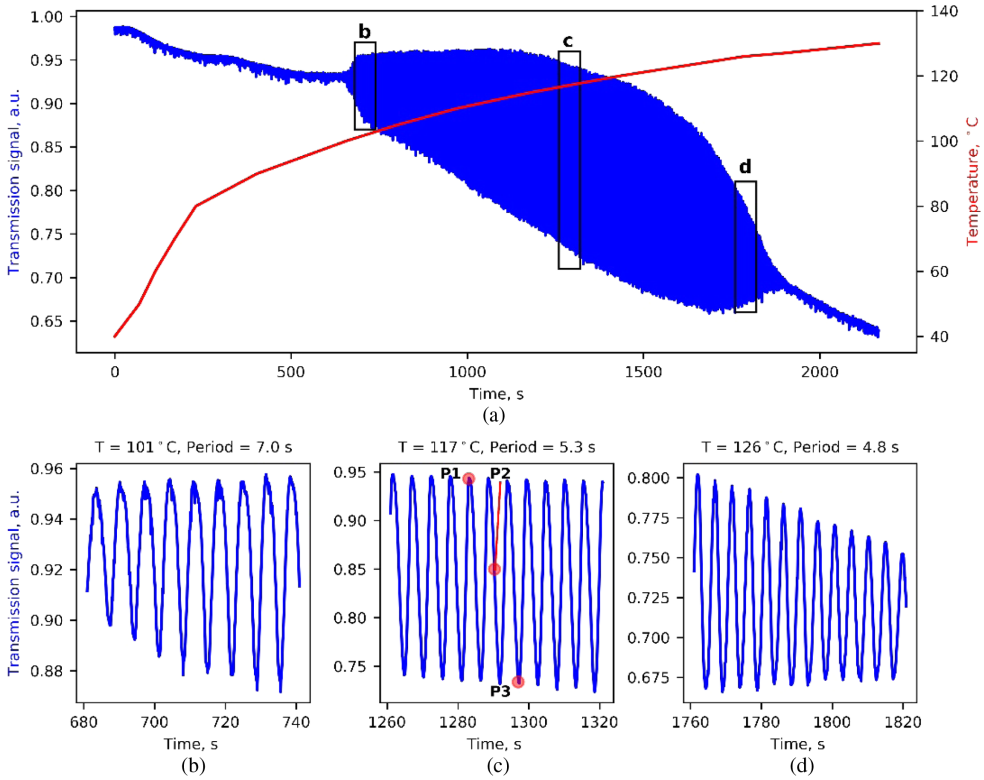

Fig. 2. Time trace of the radiation power transmitted through the Rb cell during the process of heating. Partial pressures are 150 kPa for xenon and 250 kPa for nitrogen, P1, P2, and P3, markers correspond to the time points at which the transmitted radiation spectra presented in Fig. 3(a).

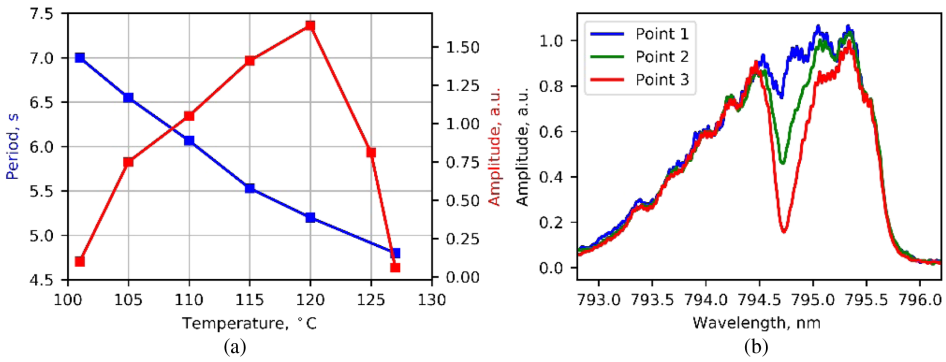

Fig. 3. (a) Dependence of oscillation period (blue curve) and amplitude (red curve) from temperature; and (b) The spectrum of radiation transmitted through the optical cell at the moments of the highest (blue curve), middle (green curve) and lowest (red curve) transmittance (points P1, P2, P3 in Fig. 2(c), respectively). A dip at the wavelength of 794.7 nm corresponds to the D1 absorption line in rubidium.

amplitude is registered after the beam was removed for 0.5–1 s and, as the duration is shortened, the amplitude becomes smaller. Switching the beam off for shorter than 0.1 s does not produce any oscillations. Another method of exciting similar transient oscillations was discovered to be switching on and off the longitudinal magnetic field, which created conditions for optical pumping of rubidium vapors and led to change in their transmittance [Fig. 4(b)]. The amplitude of oscillations then was significantly lower than that produced by the longer removal of the beam. The polarization of the incident radiation does not affect the oscillations.

Withdrawal of the phase plate and hence, switching over to linear polarization does not alter the general picture. In our work, the requirement of circular polarization is posed by the intended purpose of the experiment (production of hyperpolarized ^{129}Xe atoms). Another fact favoring the photo-induced mechanism of the discovered oscillations is the dependence of their amplitude and their mere presence upon the power of the incident radiation. As the radiation power dropped from 4–2 W at the temperature of 115°C–117°C, the oscillation amplitude was reduced at least by an order of magnitude. When the radiation power was reduced to 1.5 W, no more oscillations were observable, even though transient oscillations could still be excited by the above-mentioned methods.

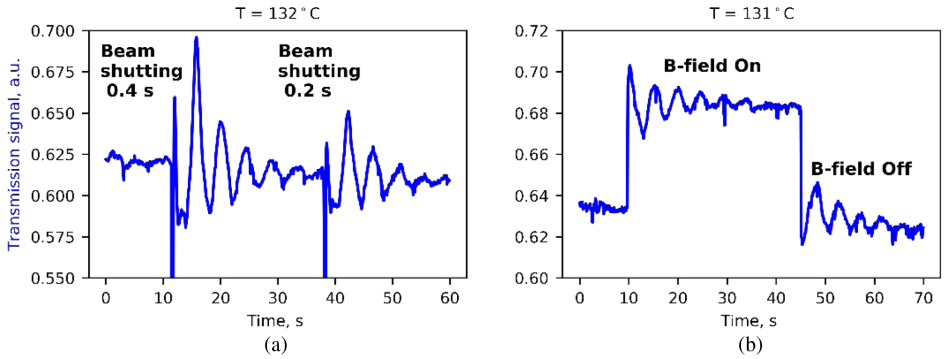

Fig. 4. Excitation of transient damped oscillations of the transmitted radiation intensity at the temperature beyond the domain where continuous oscillations occur by: (a) shutting the beam off for various amounts of time; and (b) by switching the longitudinal magnetic field on and then off.

As the partial pressure of ^{129}Xe was reduced to 120 kPa while maintaining the total gas mix pressure of 400 kPa, the oscillations could still be registered, but within a narrower temperature range from 102°C–104°C up to 117°C–120°C. This latter result was then reproduced in a different optical cell of identical design. In this case, the upper boundary of the oscillation range was found to shift down to 115°C–117°C, which may be likely explained by some error in reproduction of the gas mix (±5 kPa). At even lower partial pressures of ^{129}Xe (70–80 kPa), no oscillations emerge below 140°C, not differing in this respect from cells with pure nitrogen. These results testify that ^{129}Xe concentration affects critically the presence of the studied phenomenon and the temperature range, within which it may be observed.

4. DISCUSSION

The obtained experimental data lead to the following conclusions: oscillations of the transmitted through rubidium vapors radiation emerge within a certain temperature range depending on the xenon concentration; the amplitude and presence of these oscillations depend on the pumping radiation power; under conditions close to those required for continuous oscillations, it is possible to excite transient decaying oscillations by manipulation of the radiation power or optical absorbance of the medium; the said oscillations occur independently of the radiation polarization and direction of the external magnetic field.

Measurements of the transmitted radiation spectra indicate clearly that the transmitted intensity modulation is related to variation of absorption at the rubidium resonant line (Fig. 3). Absorption variation may arise due to several causes. First, it is variation of the concentration of single rubidium atoms. Second, transfer of rubidium atoms into a state that does not interact with radiation (something analogous to the effect of coherent population trapping [15] or optical pumping [16]. Third, narrowing or broadening of the absorption line due to impact broadening affected by gases contained in the optical cell [17–19].

The data of Figs. 2 and 4 indicate that absorption oscillates around the equilibrium state to higher and lower levels. This is why, as it seems to us, we can rule out quantum effects of atomic transfer to noninteracting states, for such effects would only result in higher transmittance and could not reduce it. Optical line narrowing could hardly be due to pressure variation inside the cell, because in this case the pressure would have to be changed by a few atm over a short period of several seconds in a gas-tight cell.

In this view, we believe that modulation of the concentration of atomic rubidium would be the most credible explanation. This may happen due to a periodic chemical reaction of rubidium with the other contents of the cell (chemical clock like Belousov–Zhabotinsky (BZ) reaction [20]) or due to physical process of rubidium dimerization (Rb_2).

In the case of chemical reaction, because the effect depends upon the ^{129}Xe concentration, it would be logical to assume interaction of rubidium with ^{129}Xe, but ^{129}Xe is a noble gas, and the possibility of its interaction with alkali metals is only discussed theoretically and at very elevated pressures (> 10 GPa) [21]. It would be pertinent here to point out the observed photo-induced character of the effect, that is its connection with excitation of rubidium atoms. This probably affects the reactivity of rubidium, and one may recall here other earlier discovered photo-induced oscillatory reactions [22]. A theory may be also advanced that in the experimental conditions Rb interacts with N_2 or other substances that may be present in the volume of the cell, in particular Ti vapor (the material of the reflector) or other vapors emitted by the fluoroplastic stopper, and in this process heavy ^{129}Xe atoms somehow exert influence upon the interaction kinetics as a catalyst. Interaction with borosilicate glass, which is the cell material, is possible under the experimental conditions [23], but it is unlikely that, namely, such interaction could lead to the observed oscillations, because at temperatures below 200°C, high voltage (over 2 kV) is necessary for extraction of free ions from the glass thickness. In our case, one would rather expect reactions taking place on the media interface, which could result in intensity modulation of the transmitted radiation independently of its wavelength.

Dimerization of rubidium, that is formation of two-atom Rb_2 molecules from single atoms, seems more realistic on the one hand, because dimer formation is possible within the established temperature range, albeit in low concentrations [24], and it may be conjectured that optical excitation of rubidium atoms may affect the dimerization process in the presence of heavy ^{129}Xe atoms. On the other hand, the measurements of spectra and transmittance indicate that at comparatively low

temperatures the medium is almost totally bleached, which means that almost all the rubidium atoms enter a bound state. This is rather possible following a chemical reaction happening moreover in the condition of an excess of the other reagent. This is why we are more inclined to accept the explanation that the observed oscillations are caused by a photo-induced chemical reaction with rubidium.

5. CONCLUSION

This work presents an investigation into a parasitic effect of absorption oscillations of the resonant radiation in optical cells with rubidium vapor in the presence of xenon and nitrogen in a compact installation for polarization of ^{129}Xe atoms by spin-exchange optical pumping. This effect is observed within a range of parameters close to the operational; therefore, this work aimed at finding out the mechanism of this effect and the simplest ways of its elimination. To avoid absorption oscillations of the resonant radiation in optical cells with rubidium vapors in the presence of xenon and nitrogen in a compact installation for polarization of ^{129}Xe atoms by spin-exchange optical pumping, it is necessary to strictly follow the recommended temperature ($<100°$C) and partial pressure of ^{129}Xe (70–80 kPa).

Our findings lead to the conclusion that the discovered effect is related to oscillations of atomic rubidium vapor concentration, which perhaps arises as a result of cyclic dimerization of rubidium or a photo-induced oscillating chemical reaction of rubidium with the contents of the optical cell.

Funding. Russian Science Foundation (22-22-00264); Ministry of Science and Higher Education of the Russian Federation (FSUS-2020-0036).

Acknowledgment. The authors express their gratitude to V. I. Yudin and N. G. Naumov for insightful discussions of the observed effect. The work of S. Kobtsev (problem definition, component testing, technical designs of the device) received support of the Ministry of Science and Higher Education of the Russian Federation.

Disclosures. The authors declare no conflicts of interest.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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