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Some issues of industrial scale boron isotopes separation by the laser assisted retarded condensation (SILARC) method

K.A. Lyakhov [a], H.J. Lee [a,*], A.N. Pechen [b,c]

[a] Institute for Nuclear Science and Technology, Plasma Physics Lab, Department of Nuclear and Energy Engineering, Jeju National University, Ara-dong 1, Jeju 63243, South Korea
[b] Department of Mathematics, National University of Science and Technology MISiS, Leninsky avenue, 4, Moscow, 119049, Russia
[c] Steklov's Mathematical Institute, Gubkina, 8, Moscow, 119991, Russia

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ABSTRACT

More cheap production of boron isotopes is needed to provide further progress in nuclear engineering, microelectronics, and nuclear medicine. In this paper feasibility of boron isotopes separation scheme by laser assisted retarded condensation (SILARC) on industrial scale is investigated. Proposed industrial scale facility has a modular structure. Each module corresponds to irradiation cell with nozzle and skimmer installed on the opposite sides. BCl_3 was chosen as a target gas mixed at low molar fraction with argon carrier gas. Photo-absorption line, corresponding to $^{11}B^{35}Cl_2^{35;37}Cl$, can be excited by CO_2 laser emission line 10P(4), but corresponding to boron-10, has no overlap with CO_2 laser emission spectrum. Therefore, core gas flow will be enriched by boron-10. It is shown that continuous gas flow irradiation is preferable. In this case excitation time (gas flow length) is desirable to make as long as possible (its upper limit is constrained by optimal pressure and temperature range and condensation rate) in order to increase excitation probability. Saving of expensive laser photons is implemented by fabrication of irradiation cell as resonator. Increasing of isotope separation rate at smaller energy expenses can be provided by appropriate choice of gas flow expansion conditions, which include concentration of target gas, carrier gas choice, gas flow and ambient gas pressure and temperature. Related optimization criterion was introduced. It was found, that even at optimal conditions isotopes separation rate is rather small, which suggests, that isotope separation should be extracted iteratively. It was considered one of possible schemes for iterative isotope recovery on industrial scale. Corresponding final equilibrium isotopic concentration in product gas is rather small. Nevertheless, this method remains attractive, because energy spent per separated isotope is still significantly smaller than other prospective methods (about three times smaller than in Molecular Obliteration Laser induced Isotope Separation (MOLIS)).

1. Introduction

Reducing amount of boron has benefits in nuclear, semiconductor and medicine industries. Less amount of boric acid used a neutron poison, which is injected in coolant in wide-spread pressurized water reactors (PWR) reduces corrosion and wear of the reactor core, and, therefore, allowing longer fuel cycle and lesser maintenance cost. Less amount of boron enriched BCl_3 or BF_3 used for silicon doping allows to make doped silica matrix more isotopically uniform, and, therefore, to increase its heat conductivity, which becomes very crucial with advancing miniaturization of electronic devices, Ref. [1]. Boron nanowires, [2], and borophene (2D boron), [3], were proposed to use in such emerging field as flexible electronics because their electrical properties are robust under strain. In this case using enriched boron can improve performance of flexible, microelectronic device due to increased heat conductivity. On the same reason using isotopically enriched boron can significantly enhance solar panels efficiency due to its dependence on temperature [4,5]. Less amount of intravenously administrated boron to tumor delivering agent allows to make boron neutron capture cancer therapy (BNCT) more efficient, Refs. [6–8]. In order to synthesize boron isotopically enriched $C_2B_{10}H_{12}$, used in BNCT, B_2H_6 should be used, which can be derived from BF_3 on industrial scale. According to http://www.sigmaaldrich.com/catalog/product/sigma, prices for enriched and unenriched products are drastically different (price for unenriched boric acid per gram is just $0.068, while for 99% enriched –$19.4). If to expect, that major contribution to this price comes from

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* Corresponding author.
E-mail addresses: lyakhov2000@yahoo.com (K.A. Lyakhov), hjlee@jejunu.ac.kr (H.J. Lee), pechen@mi.ras.ru (A.N. Pechen).

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electricity consumption, then, according to the model of industrial scale isotope separation by SILARC method, given below, this price can be reduced in three times.

Traditionally, two methods for industrial scale separation of boron isotopes are employed. The first one depends on the chemical exchange reaction and fractional distillation of the anisole, dimethyl- or diethyl-ether complex of BF_3, Refs. [9,10]. The second one involves the low temperature fractional distillation of BF_3 itself. Using of BF_3 and BCl_3 also looks beneficial for gas centrifuging, because of their high vapor pressure at room temperature: more than 50 bars and 166 kPa respectively [11]. However, it is not so efficient for separation of light isotopes like boron. Moreover, presence of three chlorine isotopes makes it hopeless for BCl_3. High vapor pressure of BCl_3 and BF_3 at room temperature is also beneficial for laser assisted methods, because there is no need in additional energy supply in the mixing tank to prevent target gas condensation. In contrast to previously mentioned methods, they have much higher selectivity, which relies on the individual for excited isotopomer photo-absorption spectrum. For instance, SILARC method, considered in this paper, employs CO_2 laser radiation, emission spectrum of which should match one of absorption lines of target isotopomers. $\nu_3 = 958\ \mathrm{cm}^{-1}$ vibrational line of BCl_3 matches corresponding line in CO_2 laser emission spectrum (according to Ref. [12], CO_2 laser of COHERENT series can be tuned within the range $(925.9\text{—}982.8\ \mathrm{cm}^{-1}) \cup (1021.45\text{—}1089.32\ \mathrm{cm}^{-1})$), while no one of fundamental or combinational absorption lines of BF_3 does, Ref. [13].

Laser assisted methods can be divided in two categories: the first one is dealing with atomic vapor, and the another one with target and carrier (buffer) gas mixture. Well known representative of the first one is Atomic Vapor Laser Isotope Separation (AVLIS), and of another one is molecular laser isotope separation (MLIS). Let us briefly compare available laser assisted methods on the basis of two criteria: overall efficiency of using the energy for isotope separation, and efficiency of isotopes harvesting. Laser assisted methods comprise MOLIS, Ref. [14], Chemical Reaction by Isotope Selective Laser Activation–CRISLA, Ref. [15], and selection of isotopes by laser excitation (SILEX): Condensation Repression by Isotope Selective Laser Activation (CRISLA-2) scheme (in this paper this scheme is called as SILARC), Refs. [16,17], http://www.silex.com.au/businesses/silex. All these methods are based on the selective excitation of target isotopes by the laser radiation. Selectivity is expressed via specific for different isotopomers resonant-like photon energy dependence of the photoabsorption cross section. Unfortunately, although infrared absorption in target gas can indeed be made at least highly isotopically preferential and the excited molecules can be preferentially photo-dissociated, subsequent chemical reactions in MOLIS and CRISLA methods tend to significantly limit the efficiency of the process. That is to say, when target gas is used as a feed material, chemical scrambling appears to significantly reduce the enrichment factor. Either one or two lasers can be used. One laser (IR) if the main process is selective excitation, and two lasers (IR + UV) if the main process is multiphoton dissociation or ionization. Only a few photons are needed for selective excitation in SILARC, and SILARC-2 methods in contrast to several dozens of photons required in the methods based on multi-photon dissociation (MOLIS, CRISLA) or ionization (AVLIS). Total energy consumed by compressors is normally significantly smaller than energy consumed by lasers, unless AVLIS, where required vacuum level is quite high, Ref. [1]. SILARC and SILARC-2 rely on the same physical process for isotope recovery, that is laser assisted control over condensation rate of target isotopomers. Cold walls selective condensation (SILARC-2) has three major disadvantages. Firstly, coaxial nozzle throughput is very low which makes it only attractive for medicine applications. Secondly, wall temperature should be kept at the same low temperature level in the quite narrow interval due to the specific temperature dependence of enrichment factor. Thirdly, it has strong dependence on the symmetry of selectively excited molecules. Therefore, only SILARC method deserves more detailed analysis. In this method isotopes harvesting is based upon well established mass separation effect in overcooled supersonic gas flow: light species escape the gas flow core at higher rate than heavy ones. The larger mass difference the more separation effect is pronounced. In order to produce sufficient mass difference, gas flow should be irradiated by laser photons of energy specifically tuned to excitation wavelength for specific isotope. Either desired or undesired isotopomers can be selectively excited. In the simplest case overcooled gas flow can be produced by orifice in a diaphragm. However, in order to produce gas flow with uniform pressure distribution, specially profiled supersonic nozzle should be designed. Formed clusters can be eliminated from the flow either by some cold surfaces (wavy plates or walls as in SILARC-2), Refs. [17,18], or by skimmer blade as in SILARC scheme, Ref. [18]. The first experimental evidence of viability of SILARC method was demonstrated on example of sulfur isotopes separation in Ref. [19].

2. Irradiation conditions

This section is addressed to basic parameters attributed to the laser field influence on the effectiveness of enrichment. Apparently, the most important one is photoabsorption cross section. At room temperature polyatomic molecules feature broad electronic absorption bands and, therefore, demonstrate low spectral selectivity to laser excitation. However, spectrum is significantly simplified because line broadening can be significantly diminished by letting diluted gas to supersonically expand. Laser frequency should be tuned to the specific vibrational mode of excited isotopomer ν_f.

Let us see now how closely match spectral characteristics of BCl_3 absorption and CO_2 laser emission. BCl_3 has strong absorption line corresponding to ν_3 fundamental vibrational mode. This spectral line for BCl_3 in gaseous state has maximum at ${}^{11}\nu_3 = 958\ \mathrm{cm}^{-1}$, corresponding to boron-11, while for boron-10, it has maximum at ${}^{10}\nu_3 = 997\ \mathrm{cm}^{-1}$, [20]. This spectral line for BCl_3 in solid state is blue-shifted from the gaseous state by $10\ \mathrm{cm}^{-1}$ (this shift is solute matrix and temperature dependent, Ref. [21]). Only emission lines, corresponding to boron-11, can be overlapped by vibration-rotation transition line 10P(4) of CO_2 laser. In order to know laser energy, that can be used at this wavelength, one needs to know laser spectrum $I_0^\nu = I_0\kappa(\nu)$. For instance, laser of series COHERENT, having maximal power 50 W at 9.23 μm, can emit light at this frequency with intensity just 7 W (extrapolated value) [12]. In this case, its value is $\kappa({}^{11}\nu_3) = 7/50$. Single photon (linear) absorption cross section can be extracted from experimental linear absorbance spectrum reported in Ref. [21]: $\sigma_A(k_{ph} \sim 1) = 13.75$ Mb.

According to the transport model for isotope separation formulated by Jeff Eerkens in [18], enrichment factor and product cut grow with laser intensity due to increase of excitation rate, but SILARC method is valid if laser intensity does not induce multiphoton dissociation/ionization. Laser excitation rate of monomers by selective photoabsorption is given by

$$k_A(\vec{r}, x, z) = \sigma_0 \phi_I(\vec{r}, x, z),\ \mathrm{s}^{-1}\ \text{per molecule}, \tag{1}$$

where photon flux density distribution is given by

$$\phi_I = \phi_\epsilon / \epsilon_L, \tag{2}$$

where $\epsilon_L = h\nu_f$, and