

# Laser separation of nitrogen isotopes by the IR + UV dissociation of ammonia molecules

V.M. Apatin, S.A. Klimin, V.B. Laptev, V.N. Lokhman, N.-D.D. Ogurok, S.V. Pigulsky, E.A. Ryabov

**Abstract.** The separation of nitrogen isotopes is studied upon successive single-photon IR excitation and UV dissociation of ammonia molecules. The excitation selectivity was provided by tuning a CO<sub>2</sub> laser to resonance with <sup>14</sup>NH<sub>3</sub> molecules [the 9R(30) laser line] or with <sup>15</sup>NH<sub>3</sub> molecules [the 9R(10) laser line]. Isotopic mixtures containing 4.8% and 0.37% (natural content) of the <sup>15</sup>NH isotope were investigated. The dependences of the selectivity and the dissociation yield for each isotopic component on the buffer gas pressure (N<sub>2</sub>, O<sub>2</sub>, Ar) and the ammonia pressure were obtained. In the limit of low NH<sub>3</sub> pressures (0.5–2 Torr), the dissociation selectivity  $\alpha(15/14)$  for <sup>15</sup>N was 17. The selectivity mechanism of the IR + UV dissociation is discussed and the outlook is considered for the development of the nitrogen isotope separation process based on this approach.

**Keywords:** laser isotope separation, ammonia, nitrogen, UV dissociation, selectivity.

## 1. Introduction

Compounds labelled with a stable <sup>15</sup>N isotope are widely used in agricultural, biological, and biochemical studies [1]. This isotope is also promising for the development of a new highly efficient fuel for nuclear reactors [2]. Atomic energetics uses isotopes in great amounts, and therefore the development of new and highly efficient technologies for nitrogen isotope separation, which can be alternative to the existing separation methods (cryogenic rectification of NO, chemical isotopic exchange in two-phase systems [3]) or can supplement them, is an urgent problem.

Laser isotope separation based on the UV dissociation of molecules, which were preliminarily selectively vibrationally excited (two-step IR + UV dissociation), was proposed in [4, 5] and was first realised in [6] for nitrogen isotopes in ammonia molecules. The isotopic selectivity of the method is achieved by selecting the frequency of a pulsed IR laser radiation so that it excites molecules with a target isotope

from the ground vibrational state to the first vibrational level and only weakly excites molecules containing a non-target isotope. The dissociation of vibrationally excited molecules is performed by a subsequent UV pulse. Usually, the isotopic selectivity is not observed at this stage.

This method is attractive first of all because the saturation of both vibrational and electronic transitions does not require, as a rule, high laser fluences  $\Phi$ . Thus, the required values of  $\Phi_{\text{IR}}$  and  $\Phi_{\text{UV}}$  for NH<sub>3</sub> molecules are tens and hundreds of mJ cm<sup>-2</sup>, respectively (see below). This circumstance virtually removes restrictions imposed by the radiation resistance of laser and photochemical reactor windows and also allows the irradiation of large gas volumes, which is one of the key factors of the process efficiency.

The development of the method was retarded by a relatively high cost of UV laser radiation (200–300 nm). The advent of quite efficient excimer lasers and high-power narrowband excimer lamps in the last years [7] again attracted interest to the use of the two-step IR + UV dissociation of molecules for efficient isotope separation for different elements, in particular, nitrogen.

In this paper, we studied, as in [6], ammonia molecules. First, both <sup>14</sup>NH<sub>3</sub> and <sup>15</sup>NH<sub>3</sub> have absorption bands in the emission region of a CO<sub>2</sub> laser. Second, ammonia is produced on a mass scale, which is important for scaling the separation process (see, for example, [8]). Third, the main product of UV dissociation is nitrogen, which can be easily separated from the irradiated substance. In [6], only the possibility of the isotopic selectivity of the IR + UV dissociation of ammonia was demonstrated for the model <sup>15</sup>NH<sub>3</sub> : <sup>14</sup>NH<sub>3</sub> = 1 : 1 mixture, and the results obtained in this paper are not sufficient for estimating the possibility of developing the technology for laser separation of nitrogen isotopes by this method. The aim of our paper is to measure in more detail the parameters of the elementary isotope separation act and to determine their dependence on the irradiation conditions. The obtained results, their discussion, and the outlook for the development of the isotope separation process are presented below.

## 2. Experimental

The IR absorption spectrum of the  $\nu_2$  mode of ammonia consists of hundreds of vibrational–rotational lines. The structure of the spectrum was studied and interpreted for the <sup>14</sup>NH<sub>3</sub> molecule in papers [9, 10] and for <sup>15</sup>NH<sub>3</sub> in paper [11]. The absorption bands of <sup>14</sup>NH<sub>3</sub> and <sup>15</sup>NH<sub>3</sub> overlap. However, there exist several not coinciding vibra-

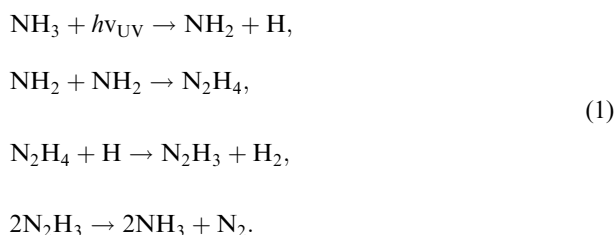
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tional–rotational lines of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  at frequencies coinciding with the emission lines of a  $\text{CO}_2$  laser. We excited  $^{14}\text{NH}_3$  molecules by the  $1084.6\text{-cm}^{-1}$   $9\text{R}(30)$  line at the  $s\text{R}(J = 5, K = 0 - 5)$  transitions, while  $^{15}\text{NH}_3$  molecules were excited by the  $1071.9\text{-cm}^{-1}$   $9\text{R}(10)$  line at the  $a\text{R}(6, 0)$  transition. The vibronic absorption spectrum of the vibrationally excited  $\text{NH}_3$  molecule considerably differs from the spectrum of this molecule in the ground state and has a maximum at a wavelength of 221.1 nm (the  $v' = 0, A \leftarrow v'' = 1, X$ ). The irradiation of  $\text{NH}_3$  molecules at 220 nm leads to its dissociation with the quantum yield close to 100 % [12]. The subsequent chemical reactions proceed in the following way [6]



It follows from this scheme that, taking into account the formation of two ammonia molecules at the last stage of the chain of reactions, the conversion of elementary nitrogen from the ammonia molecule to the nitrogen molecule is 50 %.

Our experimental setup contained a tunable pulsed  $\text{CO}_2$  laser, a UV laser source tunable in the 220-nm region, a gas cell, and photodetectors (PD in Fig. 1). The FWHM of  $\text{CO}_2$  laser pulses was 130 ns; pulses had no tails. The laser beam cross section in the irradiated region was  $\sim 0.4\text{ cm}^2$ , the intensity distribution over the beam cross section was close to Gaussian, and the pulse energy in the  $\text{TEM}_{00}$  mode achieved 100 mJ. The source of UV radiation was a XeCl laser-pumped pulsed dye laser with frequency doubling in a BBO crystal, which was tunable in the region from 210 to 260 nm (by changing dyes). The energy of the 10-ns,

211.1-nm UV pulse achieved 250  $\mu\text{J}$  in front of the cell, and the beam cross section inside the cell was  $\sim 0.025\text{ cm}^2$ . The beams were directed at a small angle to each other. The UV beam in the irradiated region was always ‘embedded’ into the IR beam. The delay between the IR and UV pulses could be continuously varied. The laser radiation parameters were controlled and measured during irradiation.

Due to a high physicochemical activity of ammonia, a special attention was paid to the preparation and analysis of samples. A vacuum system for the preparation of samples was made of stainless steel; cells of length 100 mm with internal diameter 14 mm, in which ammonia was irradiated, were made of Pyrex and sealed with fluoroplastic only. The cell windows, which were transparent both for IR and UV radiations, were made of  $\text{BaF}_2$ . The procedure was developed for the preparation of samples, which included special measures for eliminating the ‘memory’ of the equipment after the change of the isotopic composition ( $^{15}\text{NH}_3 - ^{14}\text{NH}_3$ ) of the irradiated gas. All these measures allowed us to perform correct and reproducible measurements of the elementary separation act parameters (ESAP).

The main parameters characterising the elementary separation act are the dissociation yield  $\beta_i$  (the fraction of molecules on the  $i$ th isotopic modification dissociated in the irradiated volume per laser pulse) and its selectivity  $\alpha(15/14) = \beta_{15}/\beta_{14}$ , which is defined as the ratio of the dissociation yields for different isotopomers. These parameters are usually determined from the mass spectra of the irradiated gas by measuring isotopic ratios in the initial substance and dissociation products [8]. However, we faced problems during the fulfilment of mass spectral analysis due to the partial overlap of the mass peaks of ammonia and the dissociation product (nitrogen) with the background peaks from water and nitrogen of the atmospheric air.

In this connection the dissociation yield and selectivity were determined from the IR absorption spectra of the corresponding isotopic components of ammonia measured before and after irradiation. The low-resolution ( $1.5\text{ cm}^{-1}$ )

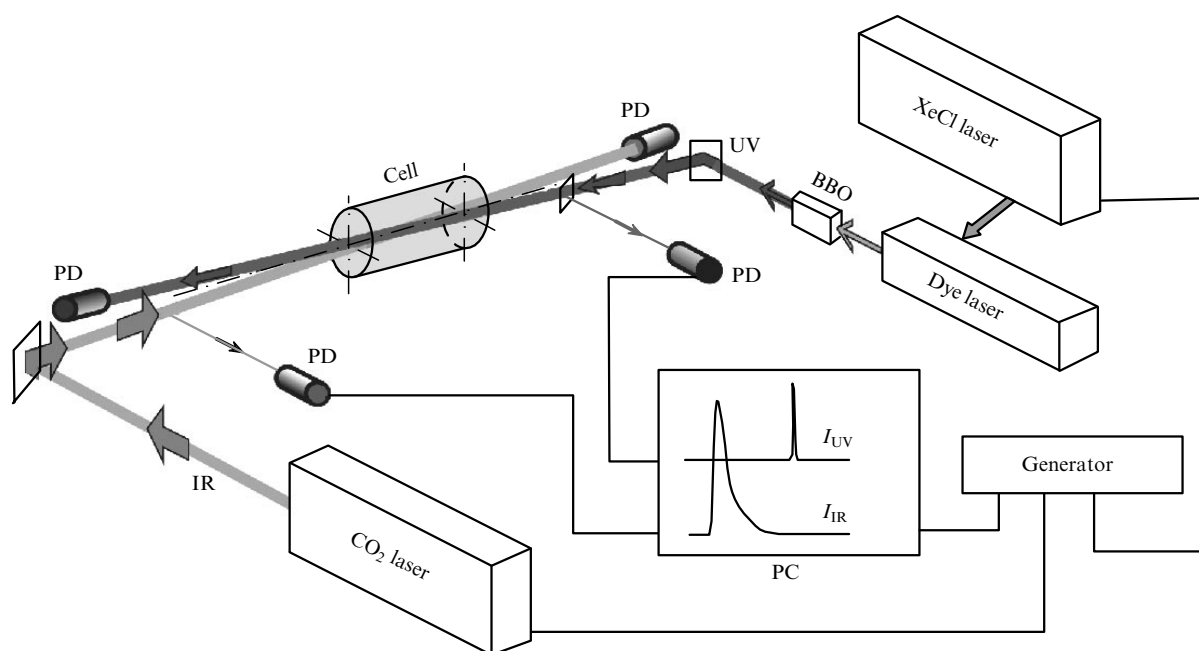


Figure 1. Scheme of the experimental setup.

IR spectra were measured in preliminary experiments with a Specord-M82 spectrophotometer. In this case, the IR absorption bands used for analyses appeared far from saturation because they represented the convolution of the profiles of individual vibrational–rotational lines and the instrumental function of the spectrophotometer. At the same time, due to a narrow width of real vibrational–rotational lines of ammonia, their peak absorption approached saturation even at low  $\text{NH}_3$  pressures (above 2 Torr). For this reason, we used the more sophisticated equipment. The dissociation yields and selectivities presented below were measured from the high-resolution IR spectra recorded before and after irradiation of a sample by using an IFS125HR Fourier spectrometer (Bruker) with the resolution 0.005–0.02  $\text{cm}^{-1}$ . At ammonia pressures 2 Torr and below, we used peaks corresponding to the aR( $J=2$ ,  $K=0-2$ ) transitions with the wave numbers 992.699, 992.450, and 991.691  $\text{cm}^{-1}$  for  $^{14}\text{NH}_3$  and 988.648, 988.396, and 987.633  $\text{cm}^{-1}$  for  $^{15}\text{NH}_3$  as the analytic IR transmission bands for both isotopic components. At higher pressures, the value of  $\beta_{14}$  was calculated by using other lines of  $^{14}\text{NH}_3$ , which were far from saturation.

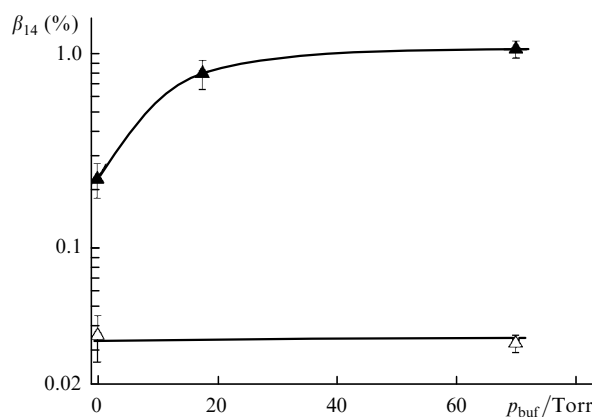
We studied mainly the two types of the isotopic mixture: the natural mixture with the initial concentration of the  $^{15}\text{N}$  isotope equal to 0.37% and the mixture enriched by  $^{15}\text{N}$  up to 4.8% ( $^{15}\text{N}:^{14}\text{N} \approx 1:20$ ). Ammonia with the natural isotopic mixture was used at the initial stage, the main  $^{14}\text{NH}_3$  component being excited by IR radiation. We measured in these experiments the parameters of the IR + UV dissociation such as the optimal delay between IR and UV radiation pulses, the saturation fluence  $\Phi_{\text{IR}}^{\text{R}}$  at the IR  $0 \rightarrow 1$  transition, and the buffer gas pressure required to overcome the ‘rotational bottleneck’ [13]. In some experiments with natural ammonia, the  $^{15}\text{NH}_3$  component was excited by the  $\text{CO}_2$  laser. We performed only several such experiments because it was difficult to measure accurately the spectra of  $^{15}\text{NH}_3$  (and, hence, ESAP) at the low concentration. For this reason, we mainly measured ESAP upon the selective dissociation of  $^{15}\text{NH}_3$  in the mixture containing 4.8% of  $^{15}\text{NH}_3$ . We hope that relaxation processes in natural ammonia and ammonia enriched by  $^{15}\text{N}$  up to 4.8% will proceed similarly.

### 3. Experimental results and discussion

The main potential advantage of laser isotope separation over classical methods is the high separation coefficient at one stage of the separation cascade (high selectivity  $\alpha$ ). The maximum ‘optical’ selectivity of the IR + UV dissociation of ammonia (assuming that the V–V and V–T relaxations are absent and the selectivity of IR excitation is infinite) is mainly determined by the thermal population of the first vibrational level with  $\nu=1$  for the non-target isotopic component. At room temperature, this level contains approximately 1% of molecules. At the UV excitation stage, isotopic effects are virtually absent, and therefore the value of  $\alpha$  is determined by the ratio of the populations of the  $\nu=1$  level for the target and non-target isotopomers. This means that the maximum value of  $\alpha$  at room temperature (18 °C) can amount to  $\sim 50$ . However, this requires the complete saturation of the  $0 \rightarrow 1$  transition in the target isotope, when the  $\nu=1$  level will contain 50% of all the molecules of the target isotope. Of course, subsequent transitions from the  $\nu=1$  level to higher-

lying levels should be also absent. However, there exists the problem of exciting the maximally possible number of molecules to the first level, because in the case of ammonia, as for many other molecules, only a small fraction  $q$  of rotational levels of the ground state interact with IR radiation, i.e. the rotational bottleneck takes place [13]. Estimates show that upon excitation of  $^{14}\text{NH}_3$  under our experimental conditions, the population of resonance rotational levels for the sR( $J=5$ ,  $K=0-5$ ) transitions is approximately 10%–14%, i.e.  $q=0.1-0.14$ , and therefore no more than 5%–7% of molecules with the target isotope can be excited to the  $\nu=1$  level. The rotational bottleneck can be eliminated by adding a sufficient amount of the buffer gas which will result in the population of depleted rotational levels due to rotational relaxation during the laser pulse  $\tau_{\text{IR}}$ . Under these conditions, when the relation  $qk_{\text{rot}}p_{\text{buf}}\tau_{\text{IR}} \gg 1$  is fulfilled ( $k_{\text{rot}}$  is the rate constant of rotational relaxation and  $p_{\text{buf}}$  is the buffer gas pressure), the saturation of the entire vibrational transition can be achieved.

Our experiments confirmed this conclusion. First we measured the dependences of the IR + UV dissociation yield for  $^{14}\text{NH}_3$  in the natural isotopic mixture on the buffer gas pressure (Ar,  $\text{N}_2$ ,  $\text{O}_2$ ). In this case, the IR radiation fluence  $\Phi_{\text{IR}}$  in all experiments was considerably higher than the corresponding saturation energy (see below). In all cases, irrespective of the gas type (curves for  $\text{N}_2$ ,  $\text{O}_2$ , and Ar virtually coincided), the dissociation yield increased monotonically and saturated with increasing buffer gas pressure (Fig. 2). In the absence of a buffer gas, preliminary IR excitation led to the increase in the dissociation yield approximately by a factor of 7, in accordance with the estimate of the population of resonance rotational levels presented above and confirms the saturation of this transition. The addition of a buffer gas at a pressure of 70 Torr resulted in the further increase in the dissociation yield by a factor of  $\sim 5$ . As a result, the maximum IR + UV dissociation yield was approximately 30 times higher than that in the absence of IR radiation, which corresponds to the IR excitation of  $\sim 30\%$  molecules. All subsequent experiments were performed by adding to ammonia a buffer gas (nitrogen) at a pressure of  $\sim 70$  Torr.



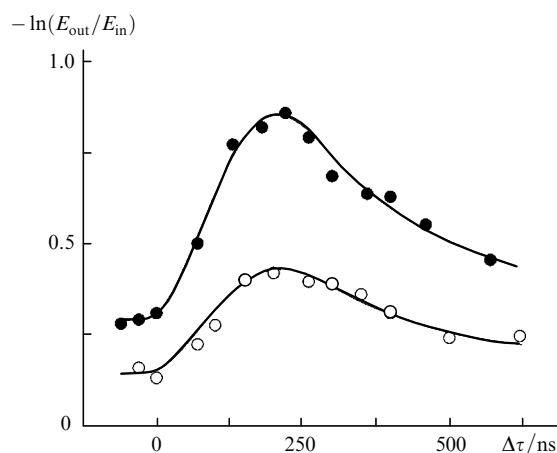
**Figure 2.** Dependences of the yield  $\beta_{14}$  of  $^{14}\text{NH}_3$  molecules on the pressure of the  $\text{N}_2$  buffer gas in the case of IR + UV dissociation ( $\blacktriangle$ ) and upon irradiation by UV light only ( $\triangle$ ). The ammonia pressure is 2 Torr, the  $^{15}\text{NH}_3$  content is 0.37% (natural),  $\Phi_{\text{IR}} = 220 \text{ mJ cm}^{-2}$ ,  $\Phi_{\text{UV}} = 9 \text{ mJ cm}^{-2}$ ,  $\Delta\tau = 200 \text{ ns}$ . The 9R(30) line is the  $\text{CO}_2$  laser line.

The maximum increase (by 50 times) in the dissociation yield when the IR field was applied was not achieved in our experiments. In our opinion, this is explained by the following reasons. First, experiments were performed at a temperature of 25 °C, when 1.11 % of molecules occupy the first vibrational level and therefore the UV dissociation yield should increase by a factor of 45 rather than by 50. Second, it seems that rotational relaxation at the buffer gas pressure of 70 Torr was not completed. Third, for the IR radiation fluence used in experiments, molecules excited due to multiphoton absorption to higher-lying levels can already play a role [14, 15].

The study of the IR + UV dissociation of  $^{15}\text{NH}_3$  in the isotopic  $^{15}\text{NH}_3 : ^{14}\text{NH}_3 \approx 1 : 20$  mixture gave the dependence of the target isotope yield on the buffer gas pressure which was similar to that presented in Fig. 2. At the same time, we found that, although the main effect of rotational relaxation was observed in the same range of buffer gas pressures (0–70 Torr), nevertheless the dissociation yield further increased with increasing pressure (approximately by 25 %) and saturation occurred at  $p_{\text{buf}} \geq 210$  Torr. The dependence of this type is probably explained by a smaller value of the factor  $q$  upon excitation of  $^{15}\text{NH}_3$  than upon excitation of  $^{14}\text{NH}_3$ .

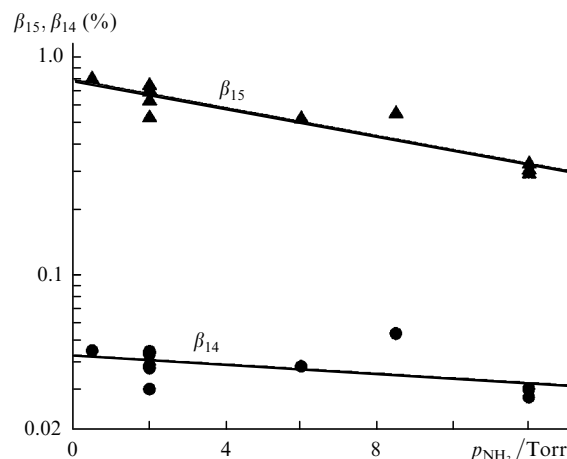
The measurements of the optimal time delay between IR and UV pulses were performed for natural ammonia and the isotopic  $^{15}\text{NH}_3 : ^{14}\text{NH}_3 \approx 1 : 20$  mixture and gave similar results. We measured the IR radiation-induced absorption of UV radiation in  $\text{NH}_3$ . Figure 3 shows the dependences of the logarithm of the ratio of the UV radiation energies at the input ( $E_{\text{in}}$ ) and output ( $E_{\text{out}}$ ) of the cell on the delay  $\Delta\tau$  between pulses for two ammonia pressures. The dependences have a maximum at  $\Delta\tau = 200$  ns. This value almost coincides with the total duration of the IR laser pulse, i.e. the maximum population of the first vibrational level in  $^{15}\text{NH}_3$  is achieved at the end of the  $\text{CO}_2$  laser pulse. It is this value of  $\Delta\tau$  that we used in subsequent isotope separation experiments.

Figures 4 and 5 present the dependences of the dissociation yield for each isotopic component and selectivity on the ammonia pressure upon excitation of  $^{15}\text{NH}_3$  in the isotopic  $^{15}\text{NH}_3 : ^{14}\text{NH}_3 \approx 1 : 20$  mixture. As the ammonia



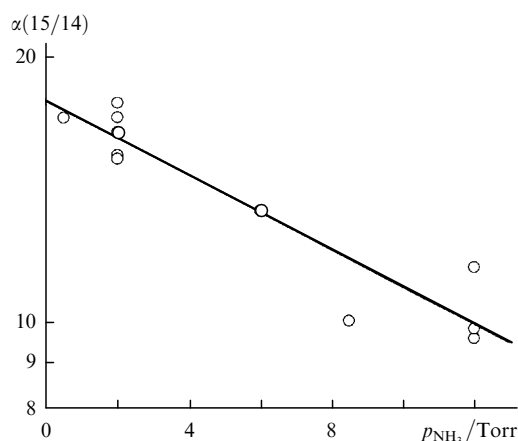
**Figure 3.** Dependences of the absorption of a UV pulse in ammonia on  $\Delta\tau$  for ammonia pressures 6 Torr (○) and 12 Torr (●). The  $^{15}\text{NH}_3$  content is 4.8 %,  $p_{\text{N}_2} = 70$  Torr,  $\Phi_{\text{IR}} = 220 \text{ mJ cm}^{-2}$ ,  $\Phi_{\text{UV}} = 9 \text{ mJ cm}^{-2}$ . The 9R(10) line is the  $\text{CO}_2$  laser line.

pressure was increased from 0.5 to 12 Torr, the yields of both isotopes monotonically decreased, but the decrease in the yield of the target isotope was considerably stronger. The decrease in the dissociation yield is explained by the deactivation of vibrationally excited ammonia molecules caused by the V–V exchange and vibrational–translational (V–T) relaxation, which has the anomalously high rate in ammonia (see review [16]).



**Figure 4.** Dependences of yields  $\beta_{14}$  and  $\beta_{15}$  of the IR + UV dissociation of  $^{14}\text{NH}_3$  (●) and  $^{15}\text{NH}_3$  (▲) molecules on the ammonia pressure. The  $^{15}\text{NH}_3$  content is 4.8 %,  $p_{\text{N}_2} = 70$  Torr,  $\Delta\tau = 200$  ns,  $\Phi_{\text{IR}} = 220 \text{ mJ cm}^{-2}$ ,  $\Phi_{\text{UV}} = 9 \text{ mJ cm}^{-2}$ . The 9R(10) line is the  $\text{CO}_2$  laser line.

The different rates of the decrease in the dissociation yield of isotopic components leads to a monotonic decrease in the selectivity with increasing ammonia pressure (Fig. 5). The extrapolation of the dependence  $\alpha = \alpha(P)$  to the zero pressure gives the maximum selectivity for  $^{15}\text{N}$  upon irradiation of the  $^{15}\text{NH}_3 : ^{14}\text{NH}_3 \approx 1 : 20$  mixture achieving 18. Note that this value is considerably smaller than the expected maximum value  $\alpha \approx 45 - 50$ . In addition, the maximum absolute dissociation yield of  $^{15}\text{NH}_3$  was 0.66 % rather than 1 %, as upon excitation of  $^{14}\text{NH}_3$  (cf. Figs 4 and 2). We assume that this is explained as follows. First, analysis of the IR absorption spectra of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  molecules showed that at the excitation frequencies used in experiments the fraction  $q$  of molecules interacting with the IR field was smaller for  $^{15}\text{NH}_3$ . Correspondingly, the saturation level of the vibrational transition at a fixed buffer gas pressure is also lower, which causes a decrease in  $\beta_{15}$ . The noticeable contribution of the effect of ‘incomplete saturation’ of the resonance  $0 \rightarrow 1$  transition is also confirmed by the measurements of the induced absorption of UV radiation in natural ammonia (6 Torr  $\text{NH}_3 + 70$  Torr  $\text{N}_2$ ). Upon the resonance IR excitation of  $^{15}\text{NH}_3$ , the absorption coefficient  $k$  for UV radiation increased by a factor of 1.36 compared to the case in the absence of IR excitation. It can be easily shown that for the selectivity  $\alpha = 17$ , the measured value of  $k$  corresponds to the population  $n_1$  of the  $v = 1$  level of  $^{15}\text{NH}_3$  equal to 0.24. Second, aside from the incomplete rotational relaxation, the depopulation of the  $v = 1$  level in  $^{15}\text{NH}_3$  can make its contribution due to multiphoton excitation mentioned above. Third, another contribution can be related to the fact that the optical selectivity of IR excitation is probably finite, which results in the increase in  $\beta_{14}$  and decrease in the



**Figure 5.** Dependence of the selectivity  $\alpha(15/14)$  of the IR + UV dissociation of  $^{15}\text{NH}_3$  molecules on the ammonia pressure. The  $^{15}\text{NH}_3$  content is 4.8 %,  $p_{\text{N}_2} = 70$  Torr,  $\Delta\tau = 200$  ns,  $\Phi_{\text{IR}} = 220$  mJ cm $^{-2}$ ,  $\Phi_{\text{UV}} = 9$  mJ cm $^{-2}$ . The 9R(10) line is the CO $_2$  laser line.

selectivity. Indeed, the 9R(10) IR line, which is resonant with the 1071.888-cm $^{-1}$  aR( $J = 6$ ,  $K = 0$ ) transition in  $^{15}\text{NH}_3$ , also falls in far wings of the aR( $J = 6$ ,  $K = 4$ , 5) bands of  $^{14}\text{NH}_3$  molecules, thereby providing the nonzero probability of excitation of this isotope.

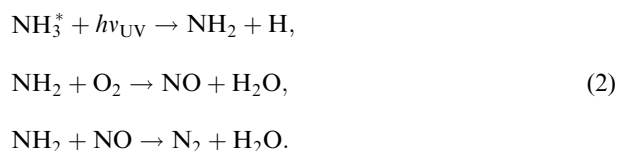
Note that the specific feature of the dependence of the selectivity on the  $\text{NH}_3$  pressure in Fig. 5 is that a high enough value of  $\alpha \approx 10$  is preserved at comparatively high (up to 12 Torr) ammonia pressures. This makes it possible, by increasing pressure, to reduce the selectivity not too much (by 1.8 times) and to enhance considerably (by 6 times) the efficiency of the process. The explanation of this comparatively weak dependence  $\alpha = \alpha(p)$  is beyond the scope of our paper and this question will be discussed elsewhere.

The selectivity of the IR + UV dissociation of ammonia can be increased by reducing the gas temperature. Thus, by using ammonia with the natural concentration of the  $^{15}\text{N}$  isotope equal to 0.37 % in the case of the selectivity  $\alpha = 18$  and a small consumption of the target component, the  $^{15}\text{N}$  content in the dissociation product can amount to  $\sim 6$  %. To double the  $^{15}\text{N}$  content, the IR + UV dissociation selectivity should be approximately doubled. This can be achieved by reducing the thermal population of the first vibrational level of the  $\nu_2$  mode for the non-target component by lowering the gas temperature from +20 °C to -70 °C. Such temperatures are provided in standard industrial refrigerators.

Note that the dissociation yield of the excited isotope under our experimental conditions did not exceed 1%. This is explained by the low intensity of UV radiation, which was much lower than the electronic-transition saturation intensity. As for the quantum yield  $\phi_{\text{UV}}$  of the UV dissociation, it proved to be higher than the expected value\*. By analysing the set of reactions (1), we see that the dissociation of four ammonia molecules should result in the production of a nitrogen molecule and two ammonia molecules i.e. the maximum value of  $\phi_{\text{UV}}$  cannot exceed 0.5. The typical

\*We define the quantum yield  $\phi_{\text{UV}}$  as the ratio of the number of ammonia molecules leaving the gas to the number of UV photons absorbed in the gas.

value of  $\phi_{\text{UV}}$  in our experiments was  $\sim 0.8$  (during the dissociation of  $^{14}\text{NH}_3$  molecules). This circumstance suggests that under our conditions (partial pressures of ammonia and buffer gas, the cell size) the scheme of secondary chemical reactions differs from scheme (1) and the composition of final products is somewhat different. This assumption is also confirmed by the fact that the dissociation yield weakly depends on the buffer gas type ( $\text{N}_2$ ,  $\text{O}_2$ , Ar, see above). It was pointed out in [6] that the photolysis of ammonia in the presence of oxygen proceeds according to the scheme



In this case, ammonia molecules in dissociation products are absent, and the ‘measured’ dissociation yield should be twice as large as in the presence of nitrogen or argon (other conditions being the same), which is inconsistent with our measurements. The influence of the experimental conditions on secondary chemical reactions, the choice of the possible acceptor of radicals, etc. are the subject of special investigations.

By using a MI-1309 magnetic static mass spectrometer, we have managed to detect nitrogen produced during the dissociation of ammonia (in mixture with argon) and measured the  $^{15}\text{N}$  enrichment in it. The qualitative conclusion of these measurements is that the conversion of elementary nitrogen from the ammonia molecule to the nitrogen molecule is close to 100 % and the produced nitrogen is enriched by  $^{15}\text{N}$ . At the same time, to overcome the difficulties encountered in experiments with ammonia, it is necessary to further improve the method of mass-spectroscopic measurements for obtaining quantitative results.

#### 4. Outlook for scaling the isotope separation process

By using the obtained experimental results, we estimate the outlook for the development of the process of nitrogen isotope separation based on the two-step IR + UV dissociation of ammonia molecules. In principle, this is a multiparametric problem (see [8]), which includes, in particular, the optimisation of the elementary separation act, the choice of the optical scheme and radiation sources, the chemical cycle, etc. In this paper, we estimate only the possible efficiency of the process and the degree of enrichment of the target  $^{15}\text{N}$  isotope. Let us first formulate the requirements for radiation at both stages.

*IR excitation.* It follows from the above discussion that, to obtain the maximum yield and selectivity of the UV dissociation, it is necessary to saturate the  $0 \rightarrow 1$  vibrational transition in the target isotope over the entire length of a photochemical reactor.

As mentioned above, to overcome the rotational bottleneck and saturate the entire vibrational transition, it is proposed to use a sufficiently high buffer gas pressure. The IR radiation fluence required in this case can be estimated. It follows from the high-resolution spectra of  $^{15}\text{NH}_3$  measured in our experiments (in the presence of nitrogen

at a pressure of 70 Torr) that the maximum of the absorption coefficient at the aR(6, 0) line is  $0.115 \text{ cm}^{-1} \text{ Torr}^{-1}$  and the corresponding absorption cross section (taking into account all molecules) is  $\sigma_{\text{tot}} = 3.23 \times 10^{-18} \text{ cm}^2$ . It follows from [13] that, if the condition  $qk_{\text{rot}} p_{\text{buf}} \tau_{\text{IR}} \gg 1$  is fulfilled, the saturation fluence for the entire transition is  $\Phi_s^{\text{IR}} = h\nu_{\text{IR}}/2\sigma_{\text{tot}}$  and amounts to  $3 \text{ mJ cm}^{-2}$ . This is the minimal estimate because the laser linewidth was not measured in our experiments. We assume that the real value of  $\Phi_s^{\text{IR}}$  is closer to  $10 \text{ mJ cm}^{-2}$ ; note that the value  $\Phi_s^{\text{IR}} \approx 16 \text{ mJ cm}^{-2}$  was obtained in [17] (however, for a different transition). In fact, the value of  $\Phi_s^{\text{IR}}$  can be even larger because our estimates neglected the finite selectivity of excitation, the V–V exchange between isotopes, etc. But in any case, we assume that the fluence  $\Phi_s^{\text{IR}} \sim 100 \text{ mJ cm}^{-2}$  is sufficient for a strong saturation of the entire vibrational transition, and such a level of the fluence flow can be readily provided by standard CO<sub>2</sub> lasers even without radiation focusing.

*UV dissociation.* The UV radiation fluence required to saturate the dissociative electronic  $v' = 0, A \leftarrow v'' = 1, X$ , transition can be estimated similarly as  $\Phi_s^{\text{UV}} = h\nu_{\text{UV}}/\sigma_{\text{UV}}$ , where  $\sigma_{\text{UV}}$  is the absorption cross section. It follows from our measurements of laser radiation absorption at a wavelength of 221.1 nm at room temperature that  $\sigma_{\text{UV}} = 8.4 \times 10^{-18} \text{ cm}^2$  and  $\Phi_s^{\text{UV}} \approx 110 \text{ mJ cm}^{-2}$ .

Let us now estimate the efficiency and other parameters of the possible process of laser separation of nitrogen isotopes by assuming that the initial content of <sup>15</sup>N is natural (0.37%). We assume for definiteness the length of a photochemical reactor is 100 cm, the cross section of the irradiated region is  $S = 1 \text{ cm}^2$ , and reactions proceed according to scheme (1), i.e. one nitrogen atom is finally produced after the dissociation of two ammonia molecules.

By using the above-presented measurements of the UV radiation absorption in ammonia after preliminary IR excitation, we obtain that for the ammonia pressure of 2 Torr in the reactor, the value  $\Phi_s^{\text{UV}} \geq 110 \text{ mJ cm}^{-2}$  will be provided over the entire reactor length at the input fluence of the reactor  $\Phi_0^{\text{UV}} \approx 220 \text{ mJ cm}^{-2}$ . In this case, 110 mJ of UV radiation, i.e. 50% of  $E_0^{\text{UV}}$  ( $E_0^{\text{UV}} = \Phi_0^{\text{UV}} S$ ) will be absorbed in the gas. Assuming that the dissociation selectivity for natural ammonia is at least no less than  $\alpha \approx 17$ , we obtain that the efficiency of the process at a laser pulse repetition rate of 100 Hz amounts to  $4.9 \times 10^{16}$  nitrogen atoms per pulse, or  $\sim 0.4 \text{ g h}^{-1}$  of nitrogen with the concentration  $x_1$  of the <sup>15</sup>N isotope equal to 5.9%. The consumption of the UV energy for obtaining one <sup>15</sup>N atom is  $\sim 0.5 \text{ keV}$ .

Note that the estimates presented above were made by using real experimental parameters. We assume that the further optimisation of irradiation conditions, in particular, the matching of the durations of IR and UV pulses and delays between them, as well as the provision of the complete saturation of the excited IR transition will allow us to increase both the selectivity and efficiency of the separation process. At the same time, the limiting selectivity of the process, as mentioned above, is mainly determined by the thermal population of the  $v = 1$  state of the non-target isotope, and the possibilities of its increasing by using the chosen scheme are restricted. One of the potential ways to overcome this restriction is the direct multiphoton IR excitation of higher vibrational levels of a target isotope (for example, the  $v = 2$  level of ammonium). A similar

approach was demonstrated earlier for the IR + UV dissociation of CF<sub>3</sub>I molecules [18], when multiphoton IR excitation was performed at the first stage.

Consider now radiation sources. The most convenient for the IR stage is a repetitively pulsed CO<sub>2</sub> laser. This is one of the most efficient and technological IR lasers, which was successfully used in the experimental industrial facility for laser separation of carbon isotopes [19]. The UV radiation at  $\sim 220 \text{ nm}$  can be obtained from KrCl lasers or excimer KrCl lamps emitting in the spectral region coinciding with the spectrum of the electronic transition in ammonia.

Excimer lamps excited by electric discharges of different types are now becoming one of the simplest UV radiation sources. The average 220-nm radiation power of KrCl lamps excited by a dc discharge or ac discharge with frequency up to  $\sim 20 \text{ kHz}$  or by long electric pulses (of duration of tens microseconds and more) achieves 1.5 kW at the efficiency  $\eta \geq 10\%$  (see, for example, [20–22]). However, despite their attractive properties, these UV sources are inconvenient for isotope separation because of a long duration of radiation pulses whose shape coincides, as a rule, with the pump pulse shape.

Light pulses with the FWHM 50–200 ns are obtained upon pumping excimer mixtures by high-voltage pulses of the corresponding duration. The light power density achieved for a volume discharge KrCl lamp with the UV preionisation was  $W \sim 0.5 \text{ kW cm}^{-2}$  in 50–200-ns pulses for the light beam diameter no less than 10 cm [23]. For barrier discharge KrCl lamps, the light power density  $W \sim 1.1 \text{ kW cm}^{-2}$  was achieved [24], i.e. the fluence was  $\Phi_{\text{UV}} \sim 12 \text{ mJ cm}^{-2}$  (the light beam diameter at the lamp output was  $\sim 8 \text{ cm}$  and the UV pulse duration was  $\sim 100 \text{ ns}$ ). According to estimates, the total power emitted within the solid angle  $4\pi$  by the lamp in [24] was  $\sim 400 \text{ kW}$  and  $\eta \sim 5\%$  for radiation emitted within the angle  $4\pi$  and  $\sim 0.6\%$  for radiation coupled out of the lamp.

Although these KrCl lamps have comparatively good energy parameters and the required emission linewidth, their use for isotope separation requires, because of the absence of spatial coherence, the development of special optical schemes for the efficient use of UV radiation. One of such schemes is the coaxial scheme of UV irradiation, which is similar to that used for the photochemical separation of mercury isotopes by radiation from mercury lamps [25]. Nevertheless, in our opinion, coherent laser radiation is more promising in principle for isotope separation than radiation from lamps.

Recent progress in the development of high-power and efficient excimer lasers almost did not concern KrCl lasers. Because of their comparatively high efficiency and specific applications, ArF, KrF and XeCl lasers were developed much better. We have failed to find information on commercially-available KrCl lasers. However, some laboratory KrCl lasers described in the literature have quite good parameters, especially when neon is used as a buffer gas in the laser mixture. In [26], 100-ns, 600 mJ laser pulses were obtained.

A laser described in [27] emitted 250 mJ in a 20-ns pulse with the total efficiency  $\eta \geq 0.8\%$  and could operate with a pulse repetition rate up to 10 Hz. The authors of [27] assume that the efficiency of the laser can be increased to 2.5%. On the other hand, an important parameter is the cost of the laser operation, which mainly depends on the frequency of the laser mixture replacement and the cost of the mixture

components. The use of the helium buffer instead of neon considerably reduces the laser operation cost; however, in this case the energy parameters of the laser are decreased. The maximum output energy of a KrCl laser with a helium-containing mixture equal to 740 mJ for  $\eta_e = 0.09\%$  was achieved in paper [28] ( $\eta_e$  is the efficiency from the energy stored in a capacitor). It seems that the best result was achieved in [29], where the efficiency  $\eta_e = 0.5\%$  was obtained for 320 mJ in a 22-ns pulse.

We can conclude that available laboratory KrCl lasers operating in a repetitively pulsed regime can be used in facilities for laser separation of nitrogen isotopes by the method of the IR + UV dissociation of ammonia molecules.

On the other hand, compounds with the  $^{15}\text{N}$  isotope concentration of 90% and higher are predominantly in demand in the market. The method considered in our paper cannot in principle provide such a high concentration per single laser enrichment stage (at least, for ammonia molecules in the excitation scheme described above). The same is obviously true for the two-stage laser process, in which ammonia synthesised from enriched nitrogen obtained at the first stage is irradiated at the second enrichment stage.

In this connection it seems promising to develop the so-called combined process in which laser enrichment is used at the first stage and one of the classical methods is used at the second stage, for example, the low-temperature rectification of NO. In this case, at the first stage the main advantage of the laser method is realised – the possibility of highly selective extraction of the minor target isotope from a raw material along with the minimal interaction of laser radiation with the main component. At the second stage, the mass raw material flows are ten times smaller than at the first stage, and therefore the use of classical methods of isotope separation is energetically and economically justified. Such a combined process was successfully used for carbon isotopes on the industrial scale (the ‘Uglerod’ complex [19, 30]). At the first stage the laser method was employed [19, 30] (multiphoton IR dissociation of  $\text{CF}_2\text{HCl}$  molecules), and at the second one – the centrifugal method.

The results obtained in our paper and the operation of the ‘Uglerod’ complex [31, 32] suggest that the combined method is promising for the separation of nitrogen isotopes. As for the economical efficiency of a large-scale process, it is determined first of all by the availability of appropriate UV radiation sources.

## 5. Conclusions

We have studied the nitrogen isotope-selective two-step IR + UV dissociation of ammonia molecules. The factors determining the mechanism of formation of the process selectivity and its efficiency have been investigated. The parameters of the elementary separation act have been determined depending on the experimental conditions. The main results of the paper are:

(i) The dependence of the selectivity on the ammonia pressure has been measured. At low  $\text{NH}_3$  pressures (0.5–2 Torr), the selectivity in  $^{15}\text{N}$  achieves  $\sim 17$ . It has been found that the selectivity  $\alpha \approx 10$  is preserved at rather high ammonia pressures (up to 12 Torr).

(ii) To overcome the rotational bottleneck effect and obtain high ESAP, it is expedient to perform the two-step ionisation of ammonia in a mixture with a buffer gas at a pressure of no less than 70–80 Torr. In this case, the 40%

dissociation yield of the target isotope can be achieved upon intense enough UV irradiation.

(iii) The obtained ESAP values confirm the possibility of the development of a large-scale process of laser separation of nitrogen isotopes by the method of two-step dissociation of ammonia by using a  $\text{CO}_2$  laser at the IR excitation stage and a KrCl laser at the UV dissociation stage. To obtain the high degree of enrichment of  $^{15}\text{N}$ , it is expedient to use a combination of the laser and classical methods of isotope separation.

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