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SEPARATION OF NITROGEN ISOTOPES WITH A LASER

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1. We report here the first high-efficiency isotope separation by a method based on two-step photodissociation of molecules. In the described experiments we separated the nitrogen isotopes ^{14}N and ^{15}N by photodissociation of the ammonia molecules $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$. Two-step molecule photodissociation was proposed [1] as a method for selective action of radiation on matter, and consists in the following. Monochromatic radiation of frequency ν_1 excites selectively a vibrational transition of molecules of only one isotopic composition. The molecules are simultaneously illuminated with light of frequency ν_2 , the quantum energy of which is sufficient for photodissociation of only the vibrationally excited molecules.

The experimental setup is shown in Fig. 1. The source of the monochromatic IR radiation of frequency ν_1 (947.74 cm^{-1}) was a pulsed CO_2 laser with transverse discharge (1). The radiation-pulse energy was 60 mJ and the pulse duration at half-height was 300 nsec. The UV source (2) at frequency ν_2 ($45\,351\text{ cm}^{-1}$) was a discharge in air ($C = 0.3\text{ }\mu\text{F}$, $U = 20\text{ kV}$). The UV pulse duration was 400 nsec at the base. The laser pulse was synchronized with the UV pulse by igniting the spark gap with a fraction ($\sim 30\%$) of the laser-beam energy focused on one of the electrodes. To eliminate completely from the continuous spark-emission spectrum the UV radiation that might have been absorbed by the unexcited NH_3 molecules in the investigate cell, an absorbing ammonia filter (3) was placed ahead of the cell. The filter was a cell with glass windows, 7.5 cm long, filled with ammonia to a pressure 1 atm. A cell (4) filled with a mixture of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ (ratio 1:1) at a total mixture pressure 20 Torr was irradiated at the frequencies ν_1 and ν_2 .

3. As shown in [2], when ammonia is pumped by a CO_2 laser, a new line appears in the electron-vibrational spectrum of NH_3 absorption, and corresponds to the transition $v' = 0 \leftarrow v'' = 1$, where v'' and v' are the vibrational numbers of the ground and excited electronic state, respectively. The frequency of the new absorption line is $45\,351\text{ cm}^{-1}$. In the described experiment, the population of the first vibrational level $v'' = 1$ of the ground electronic state of the $^{15}\text{NH}_3$ molecule was $35 \pm 5\%$ at the instant of laser-pulse action [3]. At such a population, the optical density of the ammonia in cell (4) for the new absorption line was 0.8 (cell length 3 cm). The UV radiation passing through the filter was absorbed in the new absorption line

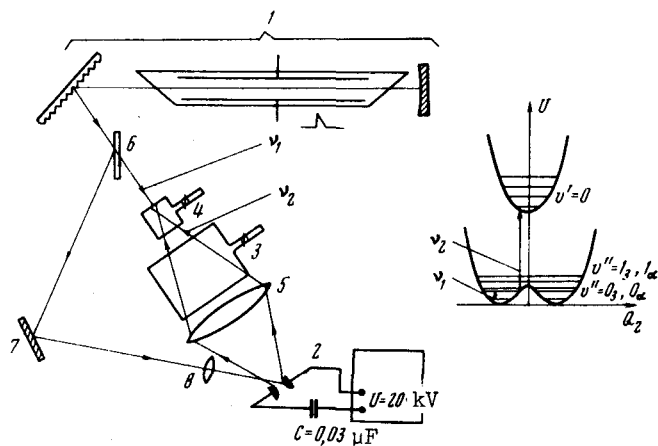


Fig. 1. Experimental setup: 1) pulsed CO_2 laser with variable emission frequency, 2) UV source, 3) absorbing ammonia filter, 4) cell with investigated gas, 5) capacitor, 6) plane-parallel plate, 7) rotary mirror, 8) focusing lens.

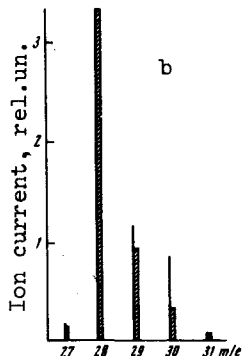
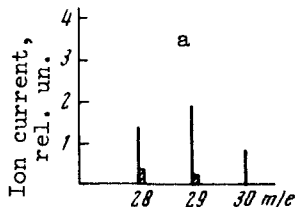
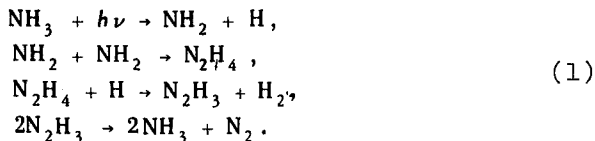


Fig. 2. Mass spectra of N_2 following nonselective photodissociation of the mixture (a) and selective two-step photodissociation of the $^{14}NH_3 + ^{15}NH_3$ mixture. The hatched lines correspond to the mass spectra of the mixture prior to irradiation (background lines).

produced in the electron-vibrational absorption spectrum of ammonia when pumped with the CO_2 laser, and caused dissociation of the vibrationally-excited molecules.

The nonselective photolysis of ammonia has been thoroughly studied in [4]. It comprises the following cycle of reactions:



We see from (1) that nitrogen is one of the end products.

We define the degree of enrichment in the reaction products (in our case N_2) with the chosen isotope (^{15}N) as the ratio of the total numbers of ^{15}N and ^{14}N atoms:

$$S_{\text{enr}} = \frac{2[^{15}N_2] + [^{14}N^{15}N]}{2[^{14}N_2] + [^{14}N^{15}N]} = \frac{2I_{30} + I_{29}}{2I_{28} + I_{29}}, \quad (2)$$

where the brackets denote the concentrations of the molecules in them; these concentrations are proportional to the intensities of the corresponding lines in the mass spectrum. In our case, in view of the statistics of the collisions, the mass-spectrum line intensity ratios always satisfy the relation

$$\frac{I_{30}}{I_{29}} = \frac{1}{4} \frac{I_{29}}{I_{28}}. \quad (3)$$

The degree of enrichment is therefore connected with the experimentally measured ratio of the line intensities I_{30} and I_{29} by the relation

$$S_{\text{enr}} = \left(2 \frac{I_{30}}{I_{29}} + 1 \right) \left(\frac{1}{2} \frac{I_{29}}{I_{30}} + 1 \right)^{-1}. \quad (4)$$

4. Two types of experiments were performed: a) First, we investigated the intensities of the ratio of the a.m.u. 29 and 30 lines for nonselective photodissociation of the ammonia isotope mixture (without laser irradiation and without the filter (3)). As expected, the intensity ratio turned out to be $I_{29}/I_{30} = 2$ within the measurement accuracy ($\pm 5\%$) (Fig. 2a).

b) Selective two-step photodissociation of the mixture of molecules $^{14}NH_3$ and $^{15}NH_3$ was produced by laser irradiation and photodissociation from the vibrationally excited state ($v'' = 1$). The line intensity ratio (after subtracting the background, shown by the hatched lines in Fig. 2, which was constant within 5%), turned out to be $I_{29}/I_{30} = 0.5 \pm 0.05$ (Fig. 2b). The attained degree of enrichment, given by (5), was $S_{\text{enr}} = 4$, i.e., the molecular nitrogen contains 80% ^{15}N atoms and 20% ^{14}N atoms if their concentrations in the initial mixture were equal.

The number of photodissociated $^{15}\text{NH}_3$ molecules is determined mainly by the intensity of the UV source and by the irradiation time. In our experiments, we dissociated several per cent of the ammonia molecules. The retention of the selectivity in the secondary chemical reaction serves as an additional confirmation that the photodissociation of ammonia follows the scheme proposed in [4].

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SPECTRUM OF DEPOLARIZED LIGHT SCATTERED IN A SOLUTION NEAR THE CRITICAL LAMINATION POINT

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The spectrum of polarized light scattered as a result of fluctuations of the entropy, pressure, and concentration, turned out to be a sensitive tool for the investigation of the most subtle processes that occur near the critical points of a pure substance and of a solution that becomes laminated (cf., e.g., [1 - 3]). There is every reason for assuming that the spectrum of light scattered as a result of anisotropy fluctuations - the Rayleigh line wing [4 - 6] - will also experience significant changes near the critical points of a pure substance or a solution.

We report here the results of the first investigation of the temperature kinetics of the Rayleigh line wing near the critical lamination point of the solution. The spectrum of the Rayleigh line wing turned out to be extremely sensitive to temperature variation when the critical point was approached, and revealed interesting singularities that were difficult to predict. We investigated solutions of nitrobenzene in n-hexane (mixture of 50% nitrobenzene by weight in n-hexane, critical lamination temperature $t_c = 20.1^\circ\text{C}$) and of aniline in cyclohexane ($t_c = 32^\circ\text{C}$). The mixture temperature was maintained constant within 0.05° (the solution was not stirred). The spectrum of depolarized scattering was excited with He-Ne laser radiation ($\lambda = 6328 \text{ \AA}$) polarized in the scattering plane; the scattered light, polarized perpendicular to the scattering plane, was observed at an angle of 90° . This light was analyzed with a Fabry-Perot interferometer with dispersion ranges 1.833 and 16.7 cm^{-1} . The variation of the spectrum of scattering by the anisotropy fluctuations is illustrated in Fig. 1, which shows the intensity distribution as a function of the frequency ν (reckoned from the exciting-line frequency) in the solution at three temperatures t ($^\circ\text{C}$) for the mixture of nitrobenzene with n-hexane. When the critical lamination point is approached (from the side of the homogeneous phase), the Rayleigh line wing narrows down rapidly and at 0.25° from the critical point it practically coincides with the apparatus function (half-width $\Delta\nu_a = 3.8 \times 10^{-2} \text{ cm}^{-1}$). We note also that the half-width of the Rayleigh line width of the mixture ($\Delta\nu_a = 3.8 \times 10^{-2} \text{ cm}^{-1}$ at 30° from the critical point) is much smaller than this half-width in pure nitrobenzene ($\Delta\nu = 0.36 \text{ cm}^{-1}$ at the same