beam refracted at the RHM/LHM interface turns out to be located at the same side from the normal to the surface as the incident beam (the so-called negative refraction). For this reason, LHMs are often called negative-refraction materials (NRMs).

Veselago's prediction has recently stimulated much theoretical interest and extensive experimental studies in search of new LHM (or NRM) materials [1 – 12]. Experimental success has been demonstrated in the microwave region [3, 6, 7]. Subsequently, however, it was shown that photonic-gap materials can also exhibit negative refraction. Similarly to the Bloch electron waves in crystals, optical waves in the periodic lattice of photonic-gap materials can have states with the opposite directions of the wave vector and the group velocity [8 – 12]. Negative refraction of light at the surface of a photonic crystal was demonstrated in a large number of numerical simulations [10 – 12].

The main attention in the studies on LHMs or NRMs has until recently been given to linear optical effects. In this report, we discuss nonlinear optical processes and show that they are also very unusual. We confine ourselves to the consideration of homogeneous NRMs and do not consider photonic-gap materials. The analysis of nonlinear optical processes in such materials is more difficult because it requires taking the optical Umklapp processes into account.

Before discussing nonlinear optical effects in NRMs, we note that two different approaches are typically used in studying the wave propagation.

One of them, based on the use of the Maxwell equations for the electric and magnetic fields **E** and **H** and the displacement vectors **B** and **D** (the so-called **E**-, **H**-, **B**-, **D**-picture) is usually applied to the investigation of the LHM electrodynamic properties. It is known, however, that this approach is applicable only in the low-frequency region because the magnetic dipole polarization density M loses its physical meaning in the high-frequency range [13]. The more general approach uses the **E**-, **B**-, **D**-picture in which $B = H$ with $\mu = 1$ and $D = \varepsilon E$, where the dielectric permittivity ε contains the entire linear response. In this approach, the dielectric tensor $\varepsilon(\omega, \mathbf{k})$ is characterized by both frequency and spatial dispersion. It is easy to see that the two approaches lead to identical results for the microwave range, where the introduction of magnetic permeability is justified. At the same time, the use of the **E**-, **B**-, **D**-picture [14] allows tracing the rise of LHMs when not only the magnetic dipole polarization but also the dielectric quadrupole one is taken into account. Moreover, it allows consistently passing to the optical wave range. The vectors **E**, **B**, and **K** then form a right-handed set in any medium, and the only nontrivial property of the so-called LHM postulated in the works of Veselago is the negative wave group velocity; therefore, negative refraction of a wave is a natural consequence of its negative group velocity [15, 16]. We have found no principal limitations on the occurrence of negative refraction in the optical wavelength range. Using the **E**-, **B**-, **D**-approach, we have discovered a number of unusual properties in negative-refraction media that emerge in studies of nonlinear optical processes, such as harmonic generation, stimulated combination (Raman) scattering, and propagation of short pulses.

We illustrate this by considering the generation of harmonics as an example. Because LHMs are normally realized in a narrow frequency range, an incident wave that occurs in this range has harmonics belonging to the frequency range where the medium exhibits positive refraction. This accounts for unusual relations between the propagation directions of the incident wave and the associated harmonics. It turns out that the harmonics generated by incident light in NRMs carry a major part of their intensity in the direction opposite to that of the incident beam propagation rather than in the direction of clear space as is typical of the generation of harmonics in ordinary media.

To conclude, we emphasize that negative refraction in the optical wavelength range can be realized in molecular crystals in the exciton resonance range (with a negative effective mass of the exciton), in gyrotropic materials, and for surface polaritons in the presence of transitional layers [17].

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Laser isotope separation by IR multiphoton dissociation of molecules

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1. Introduction

The optical separation of isotopes based on isotopic shift of electron transitions in atoms and simple molecules in the visible and ultraviolet ranges was experimentally demonstrated as early as the 1920s – 1930s. Although it was clear that infrared (IR) spectra of molecules may undergo a large isotopic shift, the practical use of this phenomenon for isotope separation was hampered by an important limitation consisting in a small change in the chemical activity of a molecule upon absorption of one IR photon, and hence a small value of the potential isotopic selectivity of an elementary process. This obstacle was overcome with the

creation of powerful IR lasers in the late 1960s and the subsequent discovery of the effect of isotopically selective IR multiphoton excitation (MPE) and dissociation (MPD) of polyatomic molecules. This talk describes the results of a research program designed to develop a laser technology for isotope separation using IR MPD of molecules, which was implemented at the Institute of Spectroscopy, Russian Academy of Sciences (jointly with a few institutions of the Ministry of Atomic Industry).

2. Isotopically selective IR MP dissociation of molecules

The essence of the IR MPD effect consists of the ability of polyatomic molecules (composed of 4–5 or more atoms) to absorb a large number (20–50) of IR quanta (up to the dissociation threshold D_0 and above) at the resonance of sufficiently intense IR radiation with one of the vibrations of these molecules. A large number of studies performed in many laboratories have demonstrated major patterns of the IR MPD process (see the review of these works in [1–3]). Multiphoton and multistep transitions in the lower part of the energy spectrum result in molecular excitation of the resonant mode states. It is at this stage that isotopic selectivity of IR MPD is largely formed. As a certain boundary value $E_{\rm bndr}$ of the vibrational energy is achieved, the vibrational motion undergoes stochastization and the so-called quasicontinuum (QC) region is formed where mode-related specificity of IR MP excitation is lost. Anharmonic interactions within the QC region give rise to fairly broad vibrational transition bands, whose width increases with increasing $E_{\rm vibr}$. This, to a large extent, makes up for the anharmonic band shift and thus ensures the possibility of further molecular excitation due to successive absorption of IR photons. As the dissociation threshold D_0 is achieved, the molecules undergo monomolecular decay, with the weakest bonds breaking, regardless of the vibration excited at the beginning of the process. IR MPD in the QC range determines the energy involved in the entire process, in particular the laser fluence threshold $\Phi_{\rm thre}$. For the majority of molecules, this value varies from 1 to 10 J cm^{-2}. The main characteristics of isotopically selective IR MPD are the dissociation yield β (the fraction of molecules dissociated per pulse in an irradiated volume) and the selectivity $\alpha = \beta_i/\beta_j$ (the ratio of the IR MPD yields of two isotopomers in a mixture).

The effect of isotopic selectivity of IR MPD was first demonstrated in experiments with BCl_3 molecules [4]. Irradiation of a mixture of $^{10}BCl_3$ and $^{11}BCl_3$ molecules with strong pulses of a CO_2-laser in the presence of oxygen resulted in intense hemiluminescence of BO^* radicals. Under resonant excitation of $^{10}BCl_3$ or $^{11}BCl_3$, predominant luminescence of $^{10}BO^*$ or $^{11}BO^*$, respectively, was observed. In these experiments, the selectivity reached the value $\alpha \approx 10$. In further experiments, sulphur isotopes ^{32}S and ^{34}S contained in the SF_6 molecule were successfully separated macroscopically [5]. Later, this effect was demonstrated for isotopes of many elements in scores of various molecules (see review [6]), with the selectivity varying from a few units in molecules that contain isotopes of heavy elements (UF_6) to $\alpha \sim 10^4$ for isotopes of hydrogen.

The prospects of using IR MPD as a new efficient method for isotope separation predetermined the initiation of a research program with the objective to study both the effect itself and the conditions conducive to high parameters of an elementary separation act (PESA), in particular, the dissociation yield and isotopic selectivity.

Based on the observed patterns of vibrational spectrum evolution of polyatomic molecules upon enhancement of their excitation, different IR MPD modalities were proposed to obtain a maximally high degree of the isotopic selectivity α and the dissociation yield β. Specifically, an MPD scheme was developed for a two-frequency IR field, with the separation of functions of isotopically selective excitation and dissociation of excited molecules [7]. Another scheme was designed for the dissociation of relatively simple polyatomic molecules in a multi-frequency field with a high boundary of vibrational quasicontinuum that ensured a large coefficient of separation (up to $\alpha \sim 10^3 - 10^4$) [8]. It was shown that the initial vibration–rotation distribution plays an important role in the formation of isotopic selectivity of IR MPD [9]. Therefore, a decrease in gas temperature results in enhanced selectivity of the process [10], which acquires special significance at small isotopic shifts.

The very first experiments on IR MPD demonstrated that as the gas pressure is increased,various collisional relaxation processes may significantly affect the PESA. Specifically, it was shown that at the usual laser pulse duration $\tau \sim 10^{-7}$ s, the selectivity α was significantly decreased (compared with its value under collisionless conditions) already in the pressure range 0.5–1 torr. We therefore carried out a series of studies aimed at elucidating the role of various relaxation processes and to search for ways to increase the working gas pressure. The principal mechanisms of the action of the vibrational $V-V$ exchange [11], rotational and $V-T$ relaxations were investigated and determined [12, 13]. In particular, it was shown that the interisotopic exchange $V-V$ plays a key role. The dependence of α on gas pressure, $\alpha = \alpha(p)$, upon excitation of the weak component ($x \ll 1$) is determined by the initial selectivity α_0. When the condition $\alpha_0 x \gg 1$ is fulfilled, α values are determined not by the total pressure but by the partial pressure of the component being excited. This allows the total gas pressure to be increased by a factor of 10 to 100. As regards the rotational and $V-T$ relaxations, their action was found to be due to the different rate of overcoming the 'rotational bottleneck' (for the former process) and the different rates of de-excitation of two isotopomers (for the latter process). These studies helped to find criteria and conditions for maintaining high selectivity at an enhanced pressure of the intrinsic gas (tens of torrs) and for raising the IR MPD yield and selectivity upon addition of a buffer gas. These findings greatly promoted practical realization of the IR MPD-based laser isotope separation (LIS) process.

3. Scaling the laser isotope separation process

Investigations into the mechanisms of elementary separation acts were paralleled by LIS scaling studies aimed at the development of an industrially suitable process. The following problems must be solved for the creation of an industrial technology:

1. The choice of the starting material and technological scheme

Both are major determinants of technical and economical characteristics of the process.

2. The source of laser radiation

A laser for the purpose must have the required energy characteristics (pulse energy 1–10 J, average power 1–10 kW) depending on the desired capacity. Moreover, it must be reliable and have a high performance coefficient.

3. The separating reactor

The reactor must ensure realization of the selected optical scheme (including the required energy fluence Φ at a given length) and maintenance of the PESA values achieved.

4. Optical elements

Optical elements must be resistant to radiation and have a long service life.

5. The chemical cycle

The chemical component of the process must ensure isolation and subsequent treatment of the concentrated product, as well as complete consumption of the starting material.

These and other problems were resolved in the course of creating the world's first demonstration system for separation of sulphur isotopes ^{34}S and ^{32}S by IR MPD of SF_6 (jointly with an affiliated center of Kurchatov Institute of Atomic Energy, now Troitsk Institute of Innovative and Thermonuclear Research) and an installation for separation of carbon isotopes on IR MPD of CF_3I and CF_3Br (jointly with the Research Institute of Stable Isotopes). The results of these studies have been summarized in monograph [14]. The principles of construction and approaches to the solution of technical problems were successfully employed for the development of an industrial process for LIS of carbon.

4. Laser separation of carbon isotopes

There are two stable isotopes of carbon, ^{13}C and ^{12}C, with the respective natural content 1.1% and 98.9%. The former isotope finds extensive application in medicine for the diagnosis of a variety of pathological conditions and in biological research. The vibration frequency of the C–F bond falls into the CO_2-laser tuning range, which predetermined the search for a working molecule amongst organofluorine compounds. The CF_2HCl molecule (freon-22) turned out to be most suitable for a large-scale LIS of carbon isotopes. The isotopic shift for the ν_3 (1107.6 cm^{-1}) and ν_8 (1127.5 cm^{-1}) bands relative to carbon isotopes amounts to $\Delta\nu_{is} \approx 20$ cm^{-1}. This facilitates tuning to the absorption band of the $^{13}CF_2HCl$ molecule and its selective dissociation by CO_2-laser radiation. The IR MPD of CF_2HCl yields CF_2 radicals that recombine to give C_2F_4:

$$^{13}CF_2HCl + nh\nu \rightarrow CF_2 + HCl\,.$$
$$\hookrightarrow C_2F_4$$

This molecule ensures high PESA values at a moderate laser fluence $\Phi = 5-10$ J cm^{-2}. The yield of the desired isotope as a result of IR MPD is (1–10)%. The selectivity can reach the values $\alpha(13/12) = 10^2-10^3$ depending on the irradiation conditions. It is important that the working pressure of CF_2HCl under these conditions may be as high as dozens of torrs. Another point of importance is the low price of freon-22, a commercially available product. After extraction of ^{13}C, freon is returned to the producer to be recycled, which solves the problem of utilization of the working material and markedly improves the economic characteristics of LIS.

An industrial LIS technology for carbon using IR MPD has been developed in Russia by joint efforts of the Institute of Spectroscopy, the Russian Research Center 'Kurchatov Institute', the State Research Center TRINITI, and the Efremov Institute of Electrophysical Apparatus. In this technology, the separating reactor is enclosed in the resonator of a transversely excited atmospheric (TEA) CO_2-laser. This arrangement makes the equivalent of a multipass absorption cuvette and ensures a high radiation utilization factor. The matching lens provides the desired Φ value in the reactor. The high gas pumping rate prevents heating of the initial material and hence a worsening of PESA. The starting material is a mixture of CF_2HCl and N_2. Nitrogen is used to protect optical elements and as a buffer gas that improves selectivity. This technology enabled the Gaz-Oil Company (Kaliningrad, Russia) to build an experimental ^{13}C-producing plant [15].

The laser-based separating block consists of a periodic-pulse TEA CO_2-laser and a separating reactor where the working mixture is irradiated. The CO_2-laser has the following characteristics: the pulse repetition rate up to 600 Hz, the pulse energy up to 3 J, and the mean power up to 1.8 kW. The irradiated mixture is fed to the rectification unit where enriched tetrafluoroethylene is extracted. In the converter, this C_2F_4 is transformed into CO_2, which is then delivered to consumers. The plant comprises three modules with the total production rate 3 g of 40% ^{13}C per hour. If necessary, further enrichment is performed by traditional methods to achieve a degree of nearly 99%. The development of an enrichment technique based on laser technology alone is underway.

5. Conclusion

The results of our studies have laid the physical and technical foundation for the laser-aided separation of isotopes using IR MPD. The newly proposed technology for separation of carbon isotopes based on IR MPD of freon-22 molecules by pulsed CO_2-lasers was employed to organize the production of enriched ^{13}C on an industrial scale. Successful implementation of the process for manufacturing carbon isotopes suggests the possibility of developing industrial technologies for separation of the isotopes of other elements.

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