

Strong mutual increase in the efficiency of isotope-selective laser IR dissociation of molecules under nonequilibrium thermodynamic conditions of the compression shock under irradiation in a bimolecular mixture

G.N. Makarov, A.N. Petin

Abstract. We have revealed a strong (by a factor of 2 to 5) mutual increase in the yield of IR molecular dissociation (by the example of CF_2HCl and CF_3Br) and a significant (by a factor of 1.5 to 3) lowering of dissociation thresholds in the nonequilibrium thermodynamic conditions of compression shock in the irradiation of the molecules by resonance IR laser radiation in the bimolecular mixture in comparison with their individual irradiation. This opens up the possibility to perform efficient isotope-selective IR dissociation of molecules at lower excitation energy densities ($\Phi \leq 1.5\text{--}2.0 \text{ J cm}^{-2}$) and thereby to improve the dissociation selectivity. This was demonstrated by the example of chlorine- and bromine-isotope selective dissociation of the specified molecules, which are characterised by quite small (less than 0.25 cm^{-1}) isotope shifts in the IR vibrational absorption spectra excited by laser radiation. The enrichment coefficients $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl}) = 0.90 \pm 0.05$ in the residual CF_2HCl gas and $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br})$ in the resultant Br_2 product are obtained when the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ molecular mixture and CF_3Br molecules, respectively, are irradiated by the 9R(30) CO_2 laser line (frequency, 1084.635 cm^{-1}) at an energy density $\Phi \approx 1.3 \text{ J cm}^{-2}$.

Keywords: clusters, molecular and cluster beams, laser spectroscopy, laser-induced selective processes.

1. Introduction

Recent years have seen numerous investigations with the use of molecular and cluster beams aimed at developing low-energy techniques of molecular laser isotope separation (MLIS) as well their alternative techniques [1–17]. The primary goal of these investigations is the search for efficient and economical methods for the isotope separation of uranium as well as of other heavy elements. The technique of IR multiphoton dissociation (MPD) of molecules [18] has been validly employed for carbon isotope separation with the use of CF_2HCl molecules [19]. The use of this technique for separating the isotopes of heavy elements is hindered by high energy consumption of the process (dissociation of the UF_6 molecule requires the absorption of approximately 40–50 photons of IR radiation with a wavelength of $16 \mu\text{m}$, i.e. about 3.2–4.0 eV), as well as by the absence of high-efficiency and

high-power laser systems and several other factors. The development of low-energy MLIS techniques and their alternatives is therefore an important and topical task. At present, the adequately studied methods of isotope-selective suppression of molecular clustering and isotope-selective dissociation of small van-der-Waals clusters [1, 2, 5–15], as well as several other less studied techniques [1, 3, 4] are considered as low-energy MLIS techniques.

As shown in Refs [1, 20], an alternative to low-energy MLIS techniques can be an approach in which isotope-selective IR dissociation of molecules is carried out under nonequilibrium thermodynamic conditions of a compression shock, which is produced in front of a solid surface in the incidence of a gas-dynamically cooled high-intensity pulsed molecular flow (beam), as well as in the stream incident on the surface. This approach was proposed and developed in Refs [21–25] in the investigation of isotope-selective IR dissociation of SF_6 [21–24] and CF_3I [25] molecules (see also review [26]).

In the excitation of SF_6 and CF_3I molecules under the nonequilibrium conditions of the compression shock produced in front of a surface, as well as in the flow incident on a surface, a high product yield and a high selectivity are achieved for a relatively low excitation energy density (below $1.5\text{--}2.0 \text{ J cm}^{-2}$), as found in Refs [21–26]. This energy density is significantly (by a factor of 3–5) lower than the energy density required for molecular dissociation in unperturbed jets and flows, and this approach may therefore be considered as an alternative to low-energy MLIS techniques [1, 20].

For SF_6 and CF_3I molecules, the respective isotopic shifts $\Delta\nu_{\text{is}}$ in the IR absorption spectra for the ν_3 (SF_6) and ν_1 (CF_3I) laser-excited vibrations amount to about 17 cm^{-1} (for the isotopes ^{32}S and ^{34}S) [27, 28] and 27 cm^{-1} (for ^{12}C and ^{13}C) [29]. These figures far exceed the linewidths of molecular IR absorption bands in a gas-dynamically cooled molecular flow. A radically different situation is realised for molecules with a small isotopic shift in the absorption bands of laser-excited vibrations, when the IR absorption spectra of different isotopomers almost completely overlap.

Recently, we undertook an investigation of selective IR dissociation under the nonequilibrium thermodynamic conditions of a compression shock for other molecules adequately studied as regards IR multiphoton excitation and dissociation, namely CF_2HCl and CF_3Br [18]. Some results obtained for these molecules are set out in Refs [16, 17]. These molecules, which contain respectively the isotopes ^{35}Cl , ^{37}Cl and ^{79}Br , ^{81}Br , are characterised by very small (less than 0.25 cm^{-1}) isotopic shifts in the absorption bands CO_2 -laser excited vibrations. Specifically, the $\Delta\nu_{\text{is}}$ shift in the ν_3 vibration

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Received 15 July 2020
Kvantovaya Elektronika 50 (11) 1036–1042 (2020)
Translated by E.N. Ragozin

($\sim 1109\text{ cm}^{-1}$) band of CF_2HCl molecules is about 0.048 cm^{-1} [30] and $\Delta\nu_{\text{is}}$ in the ν_1 vibration ($\sim 1085\text{ cm}^{-1}$) of CF_3Br molecules is 0.248 cm^{-1} [31]. The resultant data are of special interest in the context of elucidating the feasibility to apply the approach under consideration in the isotope separation for molecules with a small isotope shift in excited vibrational spectra, which is characteristic for the molecules containing the isotopes of heavy elements. For instance, for the isotopomers $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ the isotope shift in the ν_3 vibration ($\sim 627\text{ cm}^{-1}$) spectrum is also small and is 0.65 cm^{-1} [32].

Discovered in the present work was a strong mutual increase in the efficiency of isotope-selective IR laser dissociation of molecules (by the example of CF_2HCl and CF_3Br) under the nonequilibrium thermodynamic conditions of a compression shock in the irradiation of the molecules by resonance laser radiation in their bimolecular mixture in comparison with the case when they are irradiated separately. This permits one to carry out the selective IR molecular dissociation under moderate ($1.0\text{--}1.5\text{ J cm}^{-2}$) excitation energy densities and thereby improve the selectivity of the process, which is also demonstrated in our work.

We note that polyatomic molecules (SF_6 , CF_3Cl , CF_2Cl_2 etc.), which exhibit a strong absorption of high-power CO_2 -laser radiation, have been used by several authors as sensitizers for the vibrational excitation and dissociation of molecules which do not absorb CO_2 -laser radiation, including UF_6 molecules (see, for instance, paper [33] and references therein). As determined in these investigations, the transfer of laser energy absorbed by the sensitizer molecules to acceptor molecules results in a lowering of vibrational energy and dissociation yield of the sensitizer molecules [33]. Unlike these works, our investigations were performed with a mixture of molecules, in which molecules of each type resonantly absorbed the laser radiation, and in this capacity were sensitizers for another type of molecules in the mixture.

2. Thermodynamic conditions in a compression shock

The thermodynamic equilibrium between different molecular degrees of freedom is violated in the course of a rapid cooling of a molecular gas in its expansion from a nozzle. For translational, rotational, and vibrational temperatures of polyatomic molecules in the flow, the following condition is realised: $T_{1,\text{tr}} \leq T_{1,\text{rot}} \leq T_{1,\text{vib}}$ [34].

In the compression shock [35, 36] produced in the interaction of a pulsed gas-dynamically cooled molecular flow with a surface, the reverse nonequilibrium conditions are realised due to the difference between the translational, rotational, and vibrational relaxation rates [37], specifically $T_{2,\text{tr}} \geq T_{2,\text{rot}} \geq T_{2,\text{vib}}$. In this case, owing to the long vibrational–translational relaxation time (for instance, for CF_3Br $p\tau_{\text{V-T}} \approx 135\text{ }\mu\text{s Torr}$ [38] for CF_2HCl $p\tau_{\text{V-T}} \approx 65\text{ }\mu\text{s Torr}$ [39]) the vibrational temperature of the molecules in the compression shock may be hardly different from the vibrational temperature of the molecules in the incident flow when use is made of a pulsed rarefied gas flow ($T_{2,\text{vib}} \approx T_{1,\text{vib}}$). At the same time, the translational and rotational temperatures of the molecules in the compression shock are much higher than in the unperturbed flow: $T_{2,\text{tr}} > T_{1,\text{tr}}$ and $T_{2,\text{rot}} > T_{1,\text{rot}}$.

Therefore, new nonequilibrium conditions are formed in the compression shock, which are characterised by the fact that the vibrational temperature of molecules is significantly lower than the translational and rotational temperatures. It

was under precisely these conditions that we investigated the isotope-selective laser IR dissociation of CF_2HCl and CF_3Br molecules in this work. As shown by the example of SF_6 molecules in Ref. [24], the vibrational temperature has a much stronger effect on the formation of selectivity of the IR dissociation of molecules than the rotational temperature.

3. Experiment and research method

3.1. Experimental facility

The experimental facility is schematically shown in Fig. 1. It comprises a high-vacuum chamber with a pulsed molecular beam source, a quadrupole mass spectrometer (QMS) for the detection of beam particles, and a frequency-tunable pulsed CO_2 laser with a pulse energy up to 4 J for exciting molecules. The laser pulse consisted of a peak with a duration (at half maximum) of about 100 ns and a tail part with a duration of $\sim 0.5\text{ }\mu\text{s}$, which accounted for about 50% of the total pulse energy. The facility also contained a personal computer for controlling the mass spectrometer, a system for timing laser pulses to the molecular beam pulse, and a data collection and processing system. The chambers of the molecular beam source and the quadrupole mass spectrometer were pumped out by turbomolecular pumps to a pressure of no more than 10^{-5} and $\sim 10^{-7}$ Torr, respectively. Our experiments were carried out online, which made it possible to obtain information on the dissociation of molecules and the resultant products in each separate excitation pulse.

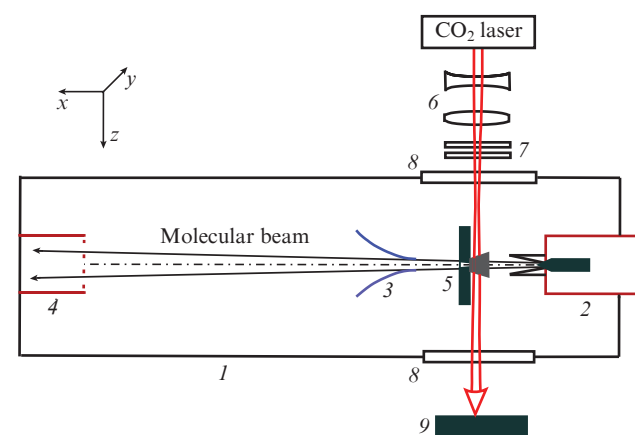


Figure 1. Schematic of the experimental facility: (1) high-vacuum chamber; (2) pulsed nozzle; (3) skimmer; (4) quadrupole mass spectrometer; (5) substrate with a truncated tetrahedral pyramid for shock wave formation; (6) cylindrical lenses; (7) attenuators; (8) NaCl windows; (9) absorber.

The beam of CF_2HCl molecules (or CF_3Br or a mixture of CF_2HCl – CF_3Br molecules) was generated in the beam source chamber as a result of the supersonic expansion of the indicated gases or their mixture through a General Valve pulsed nozzle with an outlet diameter of 0.8 mm . In order to increase the intensity of the molecular beam, a 20-mm long divergent cone with an opening angle of 15° was attached to the nozzle. The nozzle pulse repetition rate was 0.7 Hz .

The full-width-at-half-maximum duration of nozzle opening pulses varied from 350 to $475\text{ }\mu\text{s}$. The gas pressure above the nozzle was varied between 4 and 8 atm . The mass spectrometer chamber was separated from the beam source cham-

ber by a conic aperture (skimmer) approximately 1 mm in diameter located at a distance of 150 mm from the nozzle. The beam formed in this way found its way into the ionisation chamber of the QMS. The distance between the nozzle outlet section and the ionisation chamber of the QMS was 350 mm. With the help of copper mirrors and focusing cylindrical mirrors with focal distances of 240 and 180 mm, the IR laser radiation was focused and introduced into the molecular beam chamber through a NaCl window. The laser radiation crossed the molecular beam at an angle of about 90°. The laser beam measured $\sim 8 \times 6$ mm in the intersection region with the molecular beam. To maximise the molecule excitation efficiency, the CO₂-laser oscillation was tuned to a frequency of 1084.625 cm⁻¹ [the emission line 9R(30)], which was at resonance with the vibrations of CF₂HCl molecules as well as of CF₃Br molecules.

A polished metal 6-mm thick substrate 50 mm in diameter was placed at a distance $x = 50$ mm from the nozzle perpendicular to the direction of molecular flow. At the centre of the substrate there was a polished conic opening with an inlet diameter (from the nozzle side) of 1.2 mm and an outlet diameter of 5.0 mm. In the incidence of the high-intensity pulsed molecular flow on this plate, in front of it a compression shock (a shock wave) was formed [35, 36] with nonuniform, transient, and nonequilibrium condition [22, 23]. The characteristic size of the compression shock front, which is equal to the molecular free path by the order of magnitude [35, 36], amounted to 5–7 mm [22, 23, 26]. To obtain a stronger compression shock, a 12-mm high converging truncated tetrahedral pyramid was attached to the plate from the nozzle side. Two pyramid faces were made of thin NaCl plates transparent to the laser radiation. The beam molecules, as well as the products in the compression shock resulting from laser excitation and the subsequent molecular dissociation, emanated from the conic opening in the plate, made up the secondary molecular beam [22, 26], and found their way into the mass spectrometer ioniser.

3.2. Method

Laser IR dissociation of CF₂HCl molecules produces CF₂ radicals and HCl molecules. C₂F₄ molecules are produced in the subsequent recombination of CF₂ radicals [40]. The dissociation energy of CF₂HCl molecules is 47.9 ± 4.0 kcal mol⁻¹ [41]. Produced in the IR laser dissociation of CF₃Br molecules are CF₃ radicals and Br atoms, while the final products of dissociation and the subsequent chemical reactions are C₂F₆ and Br₂ molecules [42]. The CF₃Br molecule dissociation energy (66.9 ± 3.0 kcal mol⁻¹ [41]) is significantly higher than for CF₂HCl molecules. We note that both molecules comprise isotopomers: the former contains CF₂H³⁵Cl (with a content of 75% in chlorine) and CF₂H³⁷Cl (25%) isotopomers and the latter contains CF₃⁷⁹Br (with a natural content of about 50.56%) and CF₃⁸¹Br (with a content of $\sim 49.44\%$).

The dissociation yields β_{35} and β_{79} of the CF₂HCl and CF₃Br molecules were determined from intensity measurements of the time-of-flight spectra of CF₂H³⁵Cl⁺ ($m/z = 86$) molecular ions and CF₂⁷⁹Br⁺ ($m/z = 129$) ion fragments, respectively. The time-of-flight spectra of these ions were measured both without excitation of the molecules in the compression shock produced in front of the surface and with their excitation by the laser radiation. For CF₂HCl,

$$S_L = S_0(1 - \beta_{35}\Gamma), \quad (1)$$

where S_0 and S_L are the time-of-flight CF₂H³⁵Cl⁺ ion signals without and with excitation of the molecules, respectively; and Γ is the ratio between the irradiated volume and the whole volume of the molecular flow. In our experiments we analysed with the mass spectrometer the composition of only the part of molecular flow irradiated by laser radiation, and therefore $\Gamma = 1$ in our case.

The enrichment coefficient $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl})$ (enrichment with the ³⁵Cl isotope relative to ³⁷Cl) was defined as the ³⁵Cl to ³⁷Cl isotope density ratio in the residual CF₂HCl gas after irradiation relative to the similar chlorine isotope density ratio in the initial (natural) CF₂HCl gas:

$$K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl}) = \frac{1 - \beta_{35}}{1 - \beta_{37}}. \quad (2)$$

In a similar way we defined the dissociation yield β_{79} and the enrichment coefficient $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br})$ in the residual CF₃Br gas after irradiation.

In the case of CF₃Br molecules, the enrichment coefficient $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br})$ was also determined in the resultant product Br₂. Measured in experiments were the ⁷⁹Br⁷⁹Br⁺, ⁷⁹Br⁸¹Br⁺, and ⁸¹Br⁸¹Br⁺ ion signals ($m/z = 158, 160, \text{ and } 162$), which appeared in mass spectra due to the laser irradiation of the molecules. The ⁷⁹Br to ⁸¹Br atomic density ratio in the resultant Br₂ product ($R_L = ^{79}\text{Br}/^{81}\text{Br}$) was compared with the similar bromine isotope density ratio in the unirradiated molecular gas CF₃Br. Proceeding from the percentage of CF₃Br isotopomers in nature, the bromine isotope density ratio in the unirradiated CF₃Br gas ($R_0 = ^{79}\text{Br}/^{81}\text{Br}$) is ~ 1.023 . To determine the bromine isotope density ratio in the resultant Br₂ product more precisely, the experimentally measured ⁷⁹Br⁷⁹Br⁺, ⁷⁹Br⁸¹Br⁺, and ⁸¹Br⁸¹Br⁺ ion peaks were approximated by Gaussian functions. We also integrated the ion signals in the domains of the indicated mass peaks [16]. The data obtained by both techniques agree nicely with each other. The enrichment coefficient in the Br₂ product was defined as

$$K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br}) = \frac{R_L}{R_0}. \quad (3)$$

The ⁷⁹Br to ⁸¹Br atomic density ratio in the resultant Br₂ product for each fixed energy density of the exciting radiation was calculated by averaging ten intensity measurement cycles for the ion peaks of molecular bromine indicated above [16]. The chlorine isotope density ratio in the residual gas CF₂HCl–CF₃Br was determined by averaging five measured mass spectra similar to those given below (see Fig. 4).

4. Results and their discussion

Figure 2 shows the temporal dependences (time-of-flight spectra) of CF₂H³⁵Cl⁺ (Fig. 2a) and CF₂⁷⁹Br⁺ (Fig. 2b) ion signals without irradiation of the molecules in the compression shock [curve (1)] and with their irradiation by the laser pulse at the 9R (30) line (at a frequency of 1084.635 cm⁻¹) for an exciting energy density of 1.43 J cm⁻² [curves (2)]. One can see that the amplitudes of the temporal dependences of CF₂H³⁵Cl⁺ and CF₂⁷⁹Br⁺ ion signals become lower when the molecules are irradiated by the laser pulse. The differences in these amplitudes, which are proportional to the dissociation yields of the CF₂H³⁵Cl and CF₂⁷⁹Br molecules, depend on the exciting energy and are determined using relation (1) given above.

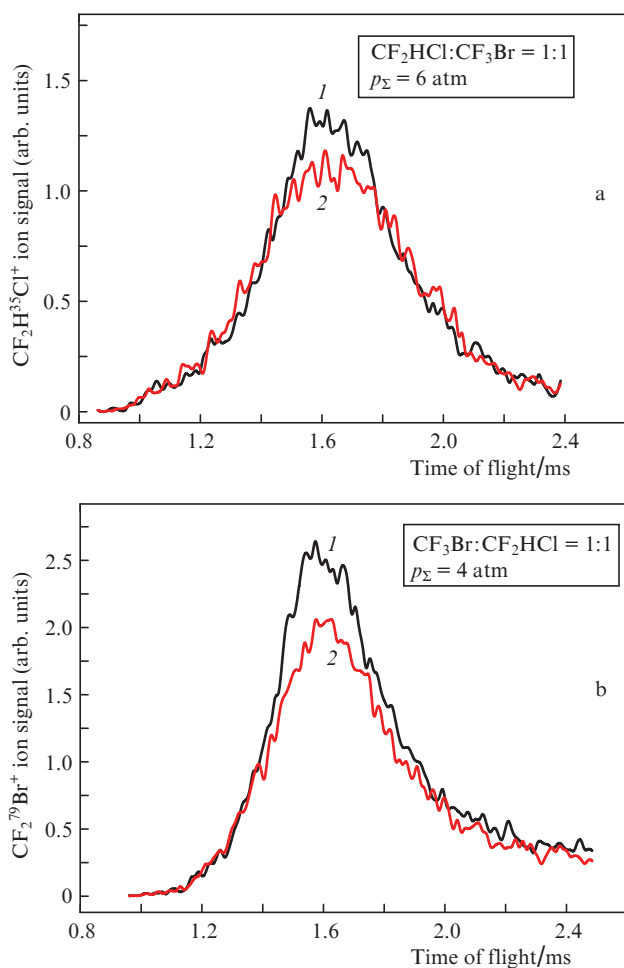


Figure 2. Time dependences (time-of-flight spectra) of (a) the $\text{CF}_2\text{H}^{35}\text{Cl}^+$ and (b) $\text{CF}_2^{79}\text{Br}^+$ ion signals without irradiation of the molecules in the compression shock (1) and with their irradiation by the laser pulse at the 9R(30) line (at a frequency of 1084.635 cm^{-1}) for an energy density of 1.43 J cm^{-2} (2). The total pressure of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ gas mixture was (a) 6.0 and (b) 4 atm. The nozzle opening pulse duration was (a) 475 and (b) 390 μs .

Figure 3a shows the $\text{CF}_2\text{H}^{35}\text{Cl}$ molecule dissociation yield β_{35} , which was measured from the $\text{CF}_2\text{H}^{35}\text{Cl}^+$ ion molecular signal, in relation to the energy density of exciting laser radiation in the irradiation of the molecules in the compression shock with the use of CF_2HCl molecular flow [curve (1)] and the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ gas mixture flow [curve (2)]. The total gas pressure above the nozzle was 4.0 atm. The molecules were excited at the 9R(30) laser line. One can see that the CF_2HCl molecule dissociation yield in a broad energy density range ($\Phi \approx 0.2\text{--}3.0\text{ J cm}^{-2}$) is significantly (by a factor of 4–7) higher in the excitation in the mixture with CF_3Br molecules than in the excitation in the absence of CF_3Br molecules. For instance, for an excitation energy density $\Phi \approx 1.5\text{ J cm}^{-2}$ the yield of CF_2HCl molecule dissociation in the former case is approximately five times higher than in the latter case. This difference is higher at lower excitation energy densities. For $\Phi \leq 1.0\text{ J cm}^{-2}$ the dissociation yield of the molecules is hardly observable in pure CF_2HCl gas, while the yield $\beta_{35} \geq 0.15$ under irradiation in the mixture with $\text{CF}_3^{79}\text{Br}$ molecules.

Figure 3b shows the $\text{CF}_3^{79}\text{Br}$ molecule dissociation yield β_{79} , which was measured from the $\text{CF}_2^{79}\text{Br}^+$ ion signal, in relation to the energy density of exciting laser radiation with the use of CF_3Br molecule flow [curve (1)] and the

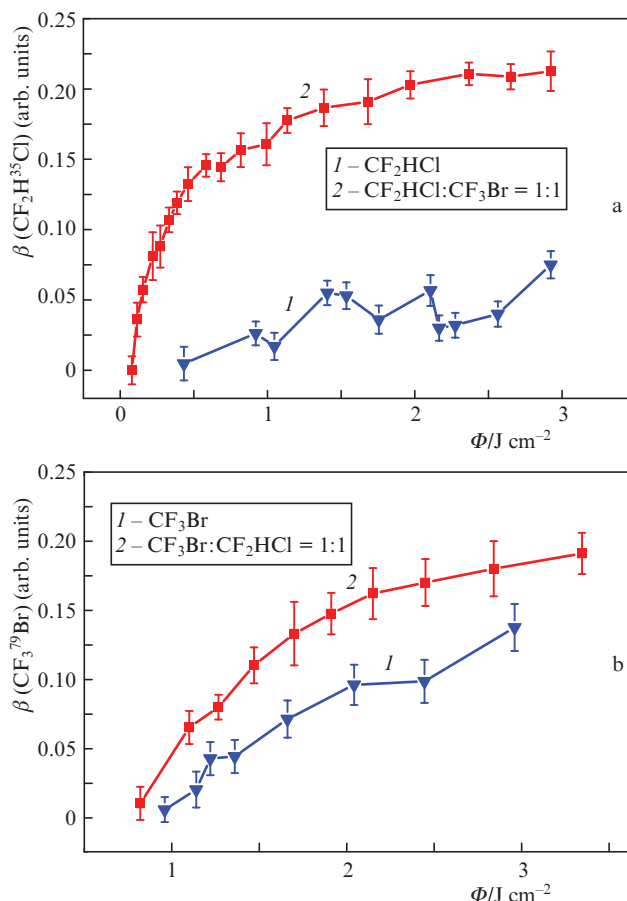


Figure 3. Dependences of molecule dissociation yield in relation to the energy density of exciting laser radiation: (a) for $\text{CF}_2\text{H}^{35}\text{Cl}$ under irradiation in the compression shock with the use of CF_2HCl molecule flow (1) and the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ gas mixture (2) and (b) for $\text{CF}_3^{79}\text{Br}$ in the irradiation of pure CF_3Br gas in the shock wave (1) and of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ gas mixture (2). The molecules were excited at the 9R(30) line. The total gas pressure above the nozzle was (a) 4 and (b) 5.2 atm. The nozzle opening pulse duration was (a) 400 and (b) 390 μs .

$\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ gas mixture [curve (2)]. The total gas pressure above the nozzle was 5.2 atm in both cases. The molecules were excited at the 9R(30) laser line. One can see that the dissociation yield of CF_3Br molecules in the energy density range under investigation ($\Phi \approx 0.75\text{--}3.0\text{ J cm}^{-2}$) is 1.5–2 times higher in the excitation in the mixture with CF_2HCl molecules than in the excitation without CF_2HCl . For $\Phi \leq 1.0\text{ J cm}^{-2}$ the dissociation of CF_3Br molecules is hardly observed in the pure stream, while their dissociation in the mixture with CF_2HCl does occur.

Note that the data shown in Fig. 3 for the molecular mixture are not normalised to the partial content of the CF_2HCl and CF_3Br molecules in the flow. In the irradiation of the mixture, the content of each type of molecules is approximately two times lower than in the case of their separate irradiation. Therefore, the dissociation yields per molecule in the molecular mixture differ even more from the dissociation yields in pure gases than follows from the data shown in the drawing.

As is clear from Fig. 3, the thresholds of IR dissociation of CF_2HCl molecules as well as of CF_3Br molecules are significantly lower when use is made of a $\text{CF}_2\text{HCl}\text{--CF}_3\text{Br}$ mixture in comparison with their separate irradiation. This is most pronounced in the dissociation of CF_2HCl molecules, whose

dissociation energy is much lower than that of the CF_3Br molecule. Specifically, the dissociation threshold of the molecules (the energy density at which the dissociation yield is $\sim 1\%$) is about 1.0 J cm^{-2} in the irradiation of pure CF_2HCl gas and about $0.15\text{--}0.2 \text{ J cm}^{-2}$ in the irradiation of the $\text{CF}_2\text{HCl}\text{--CF}_3\text{Br}$ mixture. The difference in threshold dissociation energy is appreciable smaller for CF_3Br molecules, which have a higher dissociation energy than CF_2HCl . Namely, in the irradiation of pure CF_3Br gas the dissociation threshold of the molecules is in the range $1.0\text{--}1.2 \text{ J cm}^{-2}$, while the threshold is about 0.75 J cm^{-2} in the irradiation of CF_3Br in the mixture with CF_2HCl .

The selective dissociation of CF_2HCl and CF_3Br molecules, which exhibit small isotopic shifts relative to the isotopes of chlorine and bromine in IR absorption spectra, is not realised at high excitation energy densities due to the dynamic field broadening of excited molecular transitions (Rabi frequencies). The field broadening is defined by the expression $\Delta\nu_R = \mu E/\hbar c$, where μ is the dipole transition moment; E is the electric intensity of the laser pulse; \hbar is the Planck constant; and c is the speed of light. For instance, in the dissociation of CF_3Br molecules at an excitation energy density $\Phi \approx 2.5 \text{ J cm}^{-2}$ and $\mu \approx 0.23D$ [43], the Rabi frequency $\Delta\nu_R \approx 0.53 \text{ cm}^{-1}$. It exceeds both the detuning of the laser frequency from the Q-branch frequencies of the excited transitions [16] and the isotopic shift ($\Delta\nu_{\text{is}} \approx 0.245 \text{ cm}^{-1}$) in the IR absorption spectra of $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$ molecules. Therefore, at such energy densities it is likely that both CF_3Br isotopomers are efficiently excited by the peak part of the laser pulse. In the case of CF_2HCl molecules, the isotopic shift in the spectra of excited transitions is even smaller. Consequently, the selective dissociation of these molecules may be realised only at a low excitation energy density ($\Phi \leq 1\text{--}1.5 \text{ J cm}^{-2}$).

The use of nonequilibrium thermodynamic conditions of compression shock [16] and of the effect of mutual increase in molecule dissociation efficiency in a mixture enabled us to observe the isotope-selective laser IR dissociation of the CF_2HCl and CF_3Br investigated molecules at moderate excitation energy densities.

Figure 4 shows the mass spectrum of CF_2HCl molecules in the region $m/z = 86, 87$, and 88 (the ion signals of $\text{CF}_2\text{H}^{35}\text{Cl}^+$, $\text{CF}_2^{37}\text{Cl}^+$, and $\text{CF}_2\text{H}^{37}\text{Cl}^+$, respectively) without [curve (1)] and with [curve (2)] irradiation of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ mixture by a laser pulse. The molecules were excited in the compression shock at the 9R(30) laser line frequency for an energy density $\Phi = 2.2 \text{ J cm}^{-2}$. One can see that the dissociation of $\text{CF}_2\text{H}^{35}\text{Cl}$ molecules is prevalent over the dissociation of $\text{CF}_2\text{H}^{37}\text{Cl}$ molecules.

Figure 5 shows the enrichment coefficient $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl})$ in the residual CF_2HCl gas in the irradiation of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ mixture [curve (1)] and the enrichment coefficient $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br})$ in the resultant Br_2 product in the irradiation of CF_3Br molecules [curve (2)] as functions of the energy density of exciting radiation. In both cases, the molecules were irradiated at the 9R(30) laser line (at a frequency of 1084.635 cm^{-1}). One can see that the dissociation of CF_2HCl molecules, as well as of CF_3Br molecules, is nonselective at relatively high excitation energy densities ($\Phi \geq 2.5 \text{ J cm}^{-2}$). The selective dissociation of the molecules is observed only at low excitation energy densities ($\Phi \leq 1.5\text{--}2.0 \text{ J cm}^{-2}$). For $\Phi \approx 1.3 \text{ J cm}^{-2}$, we obtained the enrichment coefficients $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl}) = 0.90 \pm 0.05$ in the irradiation of the mixture $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ and $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br}) = 1.20 \pm 0.09$ in the irradiation of CF_3Br

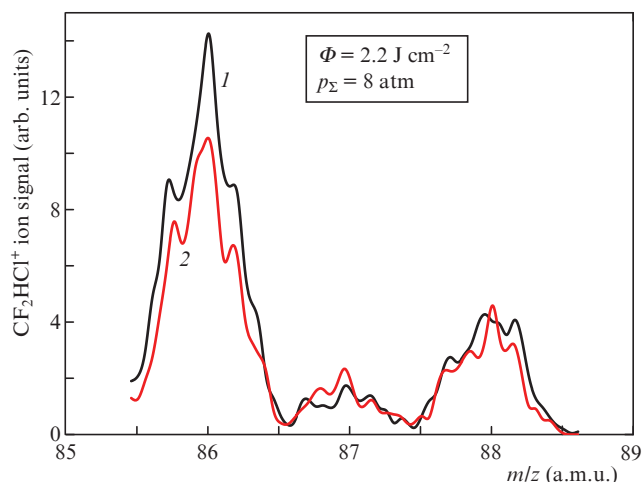


Figure 4. Mass spectra of CF_2HCl molecules ($m/z = 86, 87, 88$) before (1) and after (2) $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ mixture irradiation in the shock wave. The molecules were excited at the 9R(30) line at a laser energy density of 2.2 J cm^{-2} . The gas pressure above the nozzle is 8 atm. The duration of nozzle opening pulse is 475 μs .

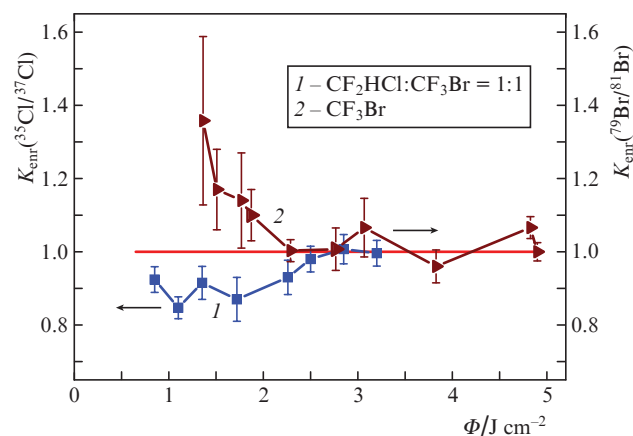


Figure 5. Enrichment coefficient $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl})$ in the residual CF_2HCl gas in the irradiation of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ molecular mixture [curve (1)] and enrichment coefficient $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br})$ in the resultant Br_2 product in the irradiation of CF_3Br molecules [curve (2)] as functions of the energy density of exciting radiation. The molecules were excited at the 9R(30) line (at a frequency of 1084.635 cm^{-1}). The gas pressure above the nozzle: (1) 8 and (2) 4 atm. The duration of nozzle opening pulse: (1) 475 and (2) 350 μs .

molecules. It also follows from Fig. 5 that the selective ionisation of CF_2HCl molecules is possible only in the mixture with CF_3Br molecules, because the dissociation of CF_2HCl molecules hardly occurs in pure gas at low excitation energy densities (see Fig. 3a).

Note that in the case of irradiation of molecules in the compression shock, a very large contribution to the total dissociation yield is made by the excitation and dissociation of molecules due to collisions that occur under a relatively high gas pressure [22, 23]. The gas density (for instance, of CF_2HCl) ρ_2 in the compression shock in front of the surface may be estimated from the relation $\rho_2/\rho_1 = (\gamma + 1)/(\gamma - 1)$, where ρ_1 is the CF_2HCl gas density in the flow incident on the surface and $\gamma = c_p/c_v = 1.18$ is the ratio of CF_2HCl specific heats [22, 23]. Estimates made taking into account the geometry of the flow showed that, under our experimental conditions (gas

pressure above the nozzle: 4.2 atm; nozzle opening pulse duration: 450 μ s; the number of molecules emanating from the nozzle per pulse: about 1.7×10^{17} , the density of molecules in the flow incident on the surface is $\sim 5.7 \times 10^{15} \text{ cm}^{-3}$ and the density in the compression shock approximately 12.1 times higher, i.e. about $6.9 \times 10^{16} \text{ cm}^{-3}$, which corresponds to a pressure of ~ 1.9 Torr. Gas densities in the compression shock comparable to the above values were also obtained in experiments with the $\text{CF}_2\text{HCl}-\text{CF}_3\text{Br}$ molecular mixture as well as with CF_3Br molecules [16].

In our opinion, it is precisely the fast collisions of excited molecules with each other, including the mutual collisions of the molecules of two types in the mixture, which are responsible, together with the radiative excitation resonant for both types of molecules, for so strong an increase in dissociation yields in comparison with the case of their separate irradiation. The nearly resonant events of fast collisional vibration–vibration energy exchange between molecules due to dipole–dipole interaction [33] as if produce, even during the course of exciting laser pulses, a very dense ‘mesh’ of populated vibrational–rotational levels consisting of the energy levels of both types of molecules. This gives rise to additional resonant channels for the excitation of molecules via a sequence of vibrational–rotational transitions of both types of molecules, which leads to their more efficient excitation up to the dissociation limit. Furthermore, the relatively high density of molecules in the compression shock and their high translational and rotations temperatures [22, 23] foster a higher-efficiency production of the final products.

5. Conclusions

A study has been made of the isotope-selective laser IR dissociation of CF_2HCl and CF_3Br molecules in the nonequilibrium conditions of the compression shock, which was produced in the interaction of a gas-dynamically cooled high-intensity pulsed molecular flow with a solid surface, under resonance IR laser irradiation of the molecules in their bimolecular mixture as well as under their separate irradiation. We have discovered a strong (2-to-5-fold) mutual increase in the dissociation yields of the molecules and a significant lowering of the dissociation thresholds in comparison with their separate irradiation.

The observed effect opens up the possibility of efficient IR laser dissociation of molecules at a moderate excitation energy density ($\Phi \leq 1.5 \text{ J cm}^{-2}$), which makes it possible to improve the selectivity of dissociation. This was demonstrated by the example of chlorine and bromine isotope-selective dissociation of the molecules under investigation. For a relatively low excitation energy density, $\Phi \approx 1.3 \text{ J cm}^{-2}$, an enrichment coefficient $K_{\text{enr}}(^{35}\text{Cl}/^{37}\text{Cl}) = 0.90 \pm 0.05$ was obtained in the irradiation of the $\text{CF}_2\text{HCl}:\text{CF}_3\text{Br} = 1:1$ molecular mixture and $K_{\text{enr}}(^{79}\text{Br}/^{81}\text{Br}) = 1.20 \pm 0.09$ was obtained in the irradiation of CF_3Br molecules at the 9R(30) line of CO_2 -laser radiation (at a frequency of 1084.635 cm^{-1}).

The resultant data give grounds to believe that the observed effect applies also to other molecules. We refer primarily to molecules containing heavy element isotopes that have a small isotopic shift in the IR absorption spectra and for which it is preferable to perform dissociation at low excitation energy densities. For instance, in the isotope-selective IR dissociation of UF_6 molecules (excited by laser radiation are the ν_3 vibrations at a frequency of about 627 cm^{-1} [27]), for a sensitizer advantage can be taken of SF_6 molecules,

which also absorb radiation in the vicinity of $16 \mu\text{m}$ (the ν_4 vibration with a frequency of about 625 cm^{-1}) [27]).

The research results show clearly that the efficiency of IR laser dissociation of molecules can be significantly improved by irradiating then in a mixture with a molecular gas that resonantly absorbs the laser radiation. The increase in the dissociation efficiency is caused by the combined action of radiative and collisional mechanisms of molecular excitation under conditions of a significant increase in the vibrational–rotational transitions of the interacting molecules, the transitions being at resonance with the laser radiation.

The results obtained, especially those concerning the observation of a strong increase in the efficiency of isotope-selective IR laser dissociation of CF_2HCl molecules in a mixture with CF_3Br molecules, in our opinion, are highly topical and important both in scientific and practical terms, since CF_2HCl molecules are used in the laser technology of carbon isotope separation in practice [19].

Acknowledgements. The authors express their appreciation to D.G. Poidashev and E.A. Ryabov for their assistance and helpful discussions. This work was partially supported by the Russian Foundation for Basic Research (Grant No. 18-02-00242).

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