

# Efficiency of selective IR multiphoton dissociation of molecules in a pulsed gas-dynamic flow interacting with a solid surface

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**Abstract.** Isotopically selective IR multiphoton dissociation of molecules ( $\text{SF}_6$ ,  $\text{CF}_3\text{I}$ ) in a pulsed gas-dynamic flow interacting with a solid surface was studied for the first time. A noticeable (severalfold) increase in the yield of products (compared to excitation of molecules in an unperturbed flow) without a substantial decrease in the selectivity of the process was observed. Possible reasons for the effect are discussed.

It has been well known for a long time that gas-dynamically cooled molecular jets and flows [1] can be used to increase the selectivity of IR multiphoton dissociation of molecules [2, 3] (see, e.g., Refs [4–6]). Due to a strong gas cooling, IR molecular absorption bands are sharply narrowed, which increases the excitation and dissociation selectivity. However, the efficiency of photochemical processes in jets and flows is low. Because of a low concentration of molecules and a low gas temperature, rates of chemical reactions, including reactions leading to the production of desired products, are low.

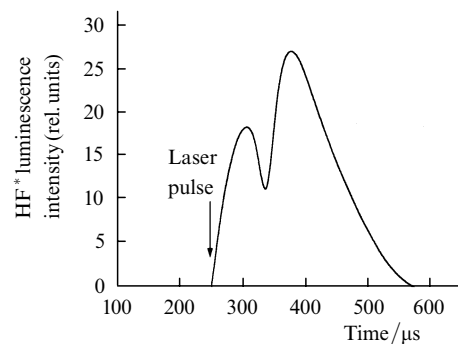
The experimental setup used in our experiments was described in detail in Refs [5, 7]. A molecular flow was formed using a pulsed ‘current loop’ type nozzle [8] with an outlet 0.75 mm in diameter. The opening time nozzle was about 100  $\mu\text{s}$  long, and the gas pressure at the input of the nozzle could be varied in the 0.1–3-atm range. The number of molecules outgoing from the nozzle in a pulse depended on the gas pressure at the input of the nozzle and was varied from  $\sim 10^{16}$  to  $\sim 10^{17}$  mol pulse $^{-1}$ . The average velocity of molecules in a flow, which was measured by the time of flight method [9], was  $420 \pm 20$  m s $^{-1}$  for  $\text{SF}_6$  and  $400 \pm 20$  m s $^{-1}$  for  $\text{CF}_3\text{I}$ .

At a distance of  $\sim 50$ –150 mm from the nozzle, we positioned a solid surface (KBr or  $\text{CaF}_2$  plates) oriented perpendicular to the flow direction. Molecules in the incident flow were excited in front of the surface, at different distances  $\Delta x$  from it, by a TEA  $\text{CO}_2$  laser pulse. The laser beam was directed perpendicular to the flow and was focused into the interaction region by a cylindrical lens, whose focal dis-

tance was 12 cm in the case of  $\text{SF}_6$  and 25 cm in the case of  $\text{CF}_3\text{I}$ . The lens axis was parallel to the surface.

We studied dissociation of molecules in a flow interacting with a surface and in an unperturbed flow (in the absence of a surface in its path). In experiments with  $\text{SF}_6$ , we measured the intensity of  $\text{HF}^*$  luminescence at  $\sim 2.5$   $\mu\text{m}$ , which accompanied dissociation of  $\text{SF}_6$  in the presence of  $\text{H}_2$  or  $\text{CH}_4$  and whose intensity was a measure of the  $\text{SF}_6$  dissociation yield [4]. We also measured the  $\text{SF}_4$  yield and its enrichment factor by the  $^{34}\text{S}$  isotope. The  $\text{HF}^*$  luminescence was measured with an IR PbS detector with a sensitive element of size  $1 \times 1$  cm. The luminescence was observed in the direction parallel to the flow. The  $\text{SF}_4$  enrichment factor was determined from the IR absorption spectra of the  $\nu_6$  molecular vibration (728  $\text{cm}^{-1}$ ), whose isotopic shift for  $^{32}\text{SF}_4$  and  $^{34}\text{SF}_4$  is  $\sim 12.3$   $\text{cm}^{-1}$  [10]. In experiments with  $\text{CF}_3\text{I}$ , we measured the  $\text{C}_2\text{F}_6$  yield and the corresponding enrichment factor for the  $^{13}\text{C}$  isotope. The measurement method is described in Ref. [5].

Fig. 1 presents a typical oscillogram of an  $\text{HF}^*$  luminescence pulse. Luminescence was observed by exciting  $\text{SF}_6$  in a mixture with  $\text{CH}_4$  ( $\text{SF}_6 : \text{CH}_4 = 1 : 1$ ) in a flow interacting with a surface. The spacing between the nozzle and the surface was 114 mm, and the distance from the excitation region to the surface was  $\Delta x = 68$  mm. The total gas pressure at the input of the nozzle was  $p = 0.7$  atm. Molecules were excited at a frequency of 947.74  $\text{cm}^{-1}$  [the 10P(16) line of the  $\text{CO}_2$  laser]. The average excitation energy fluence was  $\Phi_{\text{av}} \simeq 12$  J  $\text{cm}^{-2}$ . The laser pulse was delayed with respect to the nozzle opening pulse by the time  $\tau_d = 250$   $\mu\text{s}$ . For this delay, the laser pulse excited molecules in the flow region with the highest density.



**Figure 1.** Typical oscillogram of an  $\text{HF}^*$  luminescence pulse for  $\text{SF}_6$  excited in a mixture with  $\text{CH}_4$  ( $\text{SF}_6 : \text{CH}_4 = 1 : 1$ ) in a molecular flow interacting with a surface.

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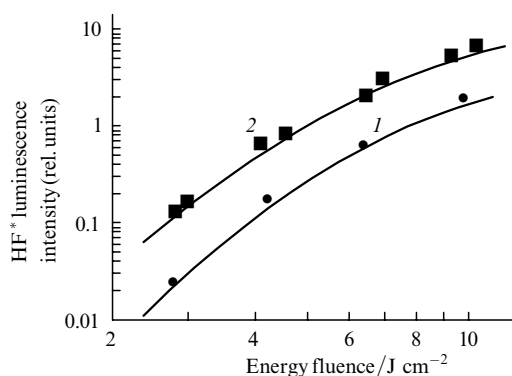
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One can see that the HF\* luminescence pulse consists of two peaks. The first peak is associated with the dissociation of molecules in the excitation region, and the second one corresponds to the dissociation of molecules in the region where the flow interacts with the surface. The time delay between the peaks increased (decreased) with increasing (decreasing) distance  $\Delta x$ . For  $\Delta x \leq 20$  mm, the peaks were not resolved in time (the IR-detector bandwidth was  $\sim 16$  kHz), but we observed a strong dependence of the HF\* luminescence intensity on the fact whether a surface was placed across the flow or not.

Fig. 2 presents the dependences of the HF\* luminescence intensity on the energy fluence averaged over the interaction region  $\Phi_{av}$  for SF<sub>6</sub> excited in a mixture with CH<sub>4</sub> (SF<sub>6</sub> : CH<sub>4</sub> = 1 : 1) in the unperturbed flow and in the flow interacting with the surface. We used a total gas pressure of 2.4 atm at the input of the nozzle, the 52-mm distance from the nozzle to the surface, and  $\Delta x = 2.5$  mm. One can see that the HF\* luminescence intensity in the flow interacting with the surface is considerably higher (by a factor of 4–5) than the intensity in the unperturbed flow. The lower the energy fluence, the larger the difference.

Results of our study of the yield of products and of their



**Figure 2.** Intensity of HF\* luminescence at the 10P(18) line of CO<sub>2</sub> as a function of energy fluence for SF<sub>6</sub> excited in a mixture with CH<sub>4</sub> (SF<sub>6</sub> : CH<sub>4</sub> = 1 : 1) in the unperturbed flow (1) and in the flow interacting with the surface (2) for a total pressure of 2.4 atm.

enrichment factors for dissociation of SF<sub>6</sub> and CF<sub>3</sub>I in the unperturbed flow and in the flow interacting with the surface are presented in the table. They were obtained for the 52-mm distance from the nozzle to the surface and  $\Delta x = 2.5$  mm. In the second case, the yield, both of SF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, is seen to be considerably higher than in the first case, whereas the selectivity (the enrichment factors of products) in the second case is only slightly lower. Note that our experiments were not aimed at obtaining the maximum selectivity.

**Table 1.** Yield of photoproducts (SF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) and their enrichment factors for dissociation of SF<sub>6</sub> and CF<sub>3</sub>I in the unperturbed flow and in the flow interacting with a surface

Molecule	Inlet pressure/atm	Laser line	Energy fluence/J cm <sup>-2</sup>	Product yield (rel. units)		Photoproduct enrichment factor	
				no surface	surface	no surface	surface
SF <sub>6</sub>	1.26	10P(16)	12	1 ± 0.2	2.7 ± 0.5	–	–
	1.26	10P(36)	10	–	–	17 ± 5	15 ± 3
CF <sub>3</sub> I	1.5	9R(10)	1.4	1 ± 0.2	2.4 ± 0.3	–	–
	1.5	9P(22)	2.6	–	–	22 ± 3	20 ± 3

Now, we briefly discuss the reasons for the effects observed in the experiments. An increase in the yield of products in a flow interacting with a surface is predominantly caused by an increase in the dissociation yield. In the case of multiphoton IR excitation, an ensemble of highly excited molecules with a rather wide distribution over vibrational levels is formed [6]. As a result, a portion of the molecules dissociates under the action of radiation, and another portion dissociates through collisions of highly excited molecules with one another [2, 6]. In an unperturbed flow, we have only photodissociation, whereas collisional dissociation of highly excited molecules, whose contribution to the total dissociation yield is commonly rather large (see, e.g., [2, 6]), is absent because of the deficiency of collisions.

In the case where a supersonic molecular flow interacts with a surface, a pressure shock is formed in front of it [11, 12], which is characterised by considerably higher values of molecular density and gas temperature in comparison with the incident flow. The limiting gas density  $\rho_2$  in the direct pressure shock is determined by the relation [11, 12]

$$\frac{\rho_2}{\rho_1} = \frac{\gamma + 1}{\gamma - 1},$$

where  $\rho_1$  is the gas density in the incident flow;  $\gamma = c_p/c_V$  is the ratio of specific heat capacities of a gas. For SF<sub>6</sub>,  $\gamma \approx 1.1$  [13], and therefore  $\rho_2/\rho_1 \approx 21$ . For CF<sub>3</sub>I,  $\gamma \approx 1.13$  [13], and we have  $\rho_2/\rho_1 \approx 16.5$ . An increase in gas temperature in a pressure shock is determined by the relation [11, 12]  $\Delta T = v^2/2c_p$ , where  $v$  is the flow velocity. For SF<sub>6</sub> with  $v \approx 420$  m s<sup>-1</sup> and  $c_p \approx 665$  J kg<sup>-1</sup> K<sup>-1</sup> [13], we have  $\Delta T \approx 130$ , and therefore in the case where the translational molecular temperature in the incident flow is  $T_1 \approx 30 - 40$  K [14], the temperature in the pressure shock is  $T_2 = T_1 + \Delta T \approx 160 - 170$  K. Owing to a high density and an increased gas temperature, highly excited molecules entering a pressure shock collide with one another, which causes an increase in dissociation yield. The selectivity of the process remains rather high because it is formed in the course of excitation of molecules in an incident cooled flow.

An increase in the yield of products may be also associated with an increase in radical concentration and the rate of chemical reactions in a pressure shock. In the particular case of CF<sub>3</sub>I studied in Ref. [15], an increase in concentration of <sup>13</sup>CF<sub>3</sub> radicals was shown to cause a strong (nearly quadratic) increase in the yield of C<sub>2</sub>F<sub>6</sub> and a substantial increase of its enrichment in the <sup>13</sup>C isotope.

Thus, one can considerably increase the efficiency of selective IR multiphoton dissociation of molecules in a pulsed gas-dynamic flow by forming a pressure shock in a flow due to its interaction with a solid surface.

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