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# TEA CO<sub>2</sub> laser-induced isotopically selective dissociation of $SF_6$ in a cold shock wave

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#### Abstract

When a pulsed gas dynamically cooled supersonic molecular flow interacts with solid surface a cold shock wave is formed in front of it, non-equilibrium conditions in which may be 'reverse' to those in the incident (unperturbed) flow. Isotopically selective infrared multiphoton dissociation of  $SF_6$  in the cold shock wave was studied. Anomalously a large increase (more than one order of magnitude) of the yield of products was found, as compared with the case of excitation of  $SF_6$  in unperturbed flow, without essential decrease of the selectivity of process. © 2000 Elsevier Science B.V. All rights reserved.

### 1. Introduction

The use of gas dynamically cooled molecular jets and flows [1] in studies of laser-induced processes including isotopically selective infrared (IR) multiphoton dissociation of molecules [2–4] is well known [2,5,6]. Due to strong cooling of the gas, the absorption bands of molecules are strongly narrowed. This results in an essential increase of the selectivity of excitation and dissociation of molecules. However, in gas dynamically cooled molecular jets and flows, the efficiency of photochemical processes is very low. Because of low temperature and small concentration of molecules in jets and flows, the rates of chemical reactions, including those resulting in the formation of desired products, are rather small. In this Letter we present the first experimental results of studies into the isotopically selective IR multiphoton dissociation of molecules (using the example of SF<sub>6</sub>) in the non-equilibrium conditions of the cold shock wave formed under interaction of a pulsed gas dynamically cooled supersonic molecular flow with solid surface. An anomalously large increase (> 10–20 times) of the yield of products was observed (compared with that in an unperturbed flow) without essential decrease of the selectivity of process.

### 2. Experimental

The experimental set-up is schematically shown in Fig. 1. The basic features of the pulsed molecular beam apparatus used in the present experiments have been previously described [6-8]. Here we will give only a brief description.

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Fig. 1. Schematic view of the experimental setup. A section in the xz-plane is shown. The laser beam is directed along the *y*-axis.

The pulsed nozzle used in the experiments was identical to one described in Ref. [9]. The nozzle outlet diameter was 0.75 mm and the opening time of the nozzle was about 100 µs (FWHM). The pressure of the gas in the nozzle could be varied from ca. 0.1 to 3 atm. The exit of the nozzle outlet had a conical shape with an angle of  $60^{\circ}$  and a cone length of 15 mm. The molecular flow was formed with the help of two thin metallic strips mounted to the exit cone. The vacuum chamber, in which the molecular flow was formed, was pumped down to  $(1-2) \times 10^{-6}$  Torr by diffusion pump. The number of molecules flowing from the nozzle in one pulse depended on the pressure above the nozzle, and in the present experiments it varied from about  $10^{16}$  up to  $10^{17}$  molecules/pulse. The mean flow velocity was measured using the time-of-flight method [7,8]. It was equal to 420 + 20 m/s.

At a distance of ~ 50–150 mm from the nozzle, a solid surface was placed perpendicular to the flow velocity direction (the plates of the KBr or CaF<sub>2</sub> crystals were used as a surface). As a consequence of the interaction between the pulsed supersonic molecular flow with a surface, a shock wave was formed in front of it [10–12] with essentially inhomogeneous, non-stationary and non-equilibrium conditions. The characteristic dimension of the front of the shock wave, which is of the order of the mean free path of the molecules [10,11], under the present experimental conditions was in the range  $\sim 0.2-5$  mm.

The molecules were excited near the surface at a distance  $\Delta x = 1.5-3$  mm from it. The laser beam was directed perpendicular to the flow direction and was focused into the interaction region by a cylindrical lens with a 12 cm focal length. The axis of the lens was parallel to the surface. The cross-section of the laser beam in the focal region of the lens was about  $0.2 \times 8.5$  mm<sup>2</sup>.

The HF<sup>\*</sup> fluorescence detection technique was used in the experiments. The HF<sup>\*</sup> fluorescence ( $\lambda \approx 2.5 \ \mu$ m) accompanies the SF<sub>6</sub> dissociation in the presence of H<sub>2</sub> or CH<sub>4</sub> [13], and its intensity correlates well with the dissociation yield of SF<sub>6</sub> [5,14]. The vibrationally excited HF<sup>\*</sup> molecules are formed in the reaction of fluorine atoms (product of SF<sub>6</sub> dissociation) with hydrogen or methane. The HF<sup>\*</sup> fluorescence was measured by non-cooled IR detector based on a PbS crystal with  $1 \times 1 \ \text{cm}^2$  active element. The yield of SF<sub>4</sub> product and the enrichment factor in it in the <sup>34</sup>S isotope were also measured. The enrichment factor in SF<sub>4</sub> was determined as:

$$K_{34}^{\text{prod}} = \begin{bmatrix} {}^{34}\text{SF}_4 \end{bmatrix} / \begin{bmatrix} {}^{32}\text{SF}_4 \end{bmatrix} \cdot \boldsymbol{\varsigma}$$
(1)

where  $[{}^{34}SF_4]/[{}^{32}SF_4]$  is the ratio of concentrations of  ${}^{34}SF_4$  and  ${}^{32}SF_4$  molecules in the product and  $s = {}^{34}S/{}^{32}S \cong 0.044$  is the ratio of concentrations of  ${}^{34}S$  and  ${}^{32}S$  in the natural SF<sub>6</sub> mixture. The concentrations of  ${}^{34}SF_4$  and  ${}^{32}SF_4$  molecules in the product were measured on the IR spectra of the  $\nu_6$  vibration of SF<sub>4</sub> (728 cm<sup>-1</sup> for  ${}^{32}SF_4$  [15]) taken with the IR spectrophotometer 'Specord 75-IR'. The isotope shift in the  $\nu_6$  vibration of SF<sub>4</sub> for  ${}^{32}SF_4$  and  ${}^{34}SF_4$  is about 12.3 cm<sup>-1</sup> [16].

## 3. Results and discussion

Fig. 2 shows the dependencies of the HF<sup>\*</sup> fluorescence intensity on the time delay  $\tau_d$  between the nozzle pulse and the CO<sub>2</sub> laser radiation pulse in the case of excitation of SF<sub>6</sub> in the mixture with CH<sub>4</sub> (SF<sub>6</sub>/CH<sub>4</sub> = 10/1) in unperturbed molecular flow (curve 1) and in the flow interacting with surface (curve 2). The total pressure of the gas above the



Fig. 2. The dependencies of the HF \*-fluorescence intensity on the time delay between the nozzle pulse and CO<sub>2</sub> laser pulse in the case of excitation of SF<sub>6</sub> in the mixture with CH<sub>4</sub> (SF<sub>6</sub>/CH<sub>4</sub> = 10/1) in unperturbed flow (curve 1) and in the flow interacting with surface (curve 2). For details see the text.

nozzle was 1 atm. The distance from the nozzle to the surface was 51 mm, and  $\Delta x = 2.5$  mm. The excitation of molecules was carried out by the 10P(16) laser line, which is in resonance with the  $\nu_3$  vibration of  ${}^{32}\text{SF}_6$  ( $\cong$  948 cm<sup>-1</sup> [17]).

One can see in the case of the excitation of SF<sub>6</sub> in the flow interacting with surface the maximum value of the HF \* fluorescence intensity is about one order of magnitude larger as compared with that in an unperturbed flow. The sharp front of the shock wave appears in the region where the molecules are excited (at a distance  $\Delta x = 2.5$  mm from the surface) at  $\tau_d \approx 370 \ \mu$ s. At smaller distances  $\Delta x$  from the surface to the excitation zone the peak of the HF \* fluorescence intensity was greater. For example, at  $\Delta x = 1.6$  mm, the front of the shock wave was observed at  $\tau_d \approx 330 \ \mu$ s and the intensity of HF \* fluorescence in the shock wave was about 20 times greater than in an unperturbed flow.

Note, in the flow interacting with a surface, the HF<sup>\*</sup> fluorescence intensity was considerably greater as compared with that in an unperturbed flow at all delay times, even if the molecules were excited not in the shock wave but rather in the incident flow (e.g., at  $\tau_d \leq 350 \ \mu$ s for the case of Fig. 2). This is connected with the following. In an unperturbed flow, the concentration of molecules is rather low ( $N \leq 10^{15} \ \text{cm}^{-3}$ ). Because of a deficit of collisions,

only radiation dissociation of molecules occurs, whereas collisional dissociation of vibrationally highly excited molecules, which usually gives an essential rise to the total dissociation yield of molecules [2,3], does not take place. In the flow interacting with a surface due to formation of a shock wave, where the concentration of molecules increases sharply, the collisional dissociation of highly excited molecules coming to the shock wave region is greatly enhanced, giving rise to the HF<sup>\*</sup> fluorescence signal.

Fig. 3 presents the dependencies of the HF<sup>\*</sup> fluorescence intensity on the CO<sub>2</sub> laser pulse energy fluence in the case of excitation of  $SF_6$  in a mixture with  $CH_4$  (SF<sub>6</sub>/CH<sub>4</sub> = 1/1) in unperturbed flow (curve 1) (there was no surface on the way of the flow), in the flow incident on the surface (curve 2), and in the shock wave (curve 3). The total pressure of the gas in the nozzle was 2.4 atm. The distance from the nozzle to the surface (for curves 2 and 3) was 51 mm,  $\Delta x = 2.5$  mm. The delay times corresponded to the maxima in the TOF spectra of  $SF_6/CH_4$  flow ( $\tau_d = 240 \ \mu s$  for curves 1 and 2, and  $\tau_{\rm d} = 310 \ \mu s$  for curve 3). One can see that the HF \* fluorescence intensity in the flow incident on the surface is about 4 times greater and in the shock wave more than 30 times greater than in unperturbed flow. The difference is even larger at  $\Phi_{av} \leq 3-4$ J/cm<sup>2</sup>, indicating increase of collisional dissociation



Fig. 3. The dependencies of the HF \*-fluorescence intensity on the  $CO_2$  laser energy fluence in the case of excitation of  $SF_6$  in the mixture with  $CH_4$  ( $SF_6/CH_4 = 1/1$ ) in unperturbed flow (curve 1), in the flow incident on the surface (curve 2), and in the shock wave (curve 3). For details see the text.

of molecules in the shock wave at low-energy fluences.

We also carried out experiments on the direct measurement of the yield of  $SF_4$  product under excitation of  $SF_6$  in unperturbed flow and in the flow interacting with surface. The method of measurement of product yield in the pulsed gas dynamic flow is described in Ref. [6,18]. In these measurements, we used a pure  $SF_6$  flow. The  $SF_4$  yield in an unperturbed flow has been measured at  $\tau_d = 260 \ \mu s$  and in the flow interacting with a surface at  $\tau_d = 260 \ \mu s$ and  $\tau_{\rm d} = 370$  µs. These delay times correspond to maxima in TOF spectra of molecules (see Fig. 2). The distance from the nozzle to the surface was 52 mm and  $\Delta x = 2.5$  mm. The SF<sub>6</sub> pressure above the nozzle was 1.25 atm. The excitation energy fluence was  $\Phi_{av} \cong 12 \text{ J/cm}^2$ . It was found that in the case of excitation of molecules in the flow incident on the surface (at  $\tau_d = 260 \ \mu s$ ) the SF<sub>4</sub> yield was 2.5 times greater, and in the shock wave (at  $\tau_d = 370 \ \mu s$ ) about 12 times greater than in unperturbed flow.

Note that similar results were also obtained by us with  $CF_3I$  molecules. The  $C_2F_6$  product yield in the shock wave was found to be about 16 times greater than in unperturbed flow.

The selectivity of the process was studied by measuring the frequency dependencies of the HF\* fluorescence intensity in the case of excitation of  $SF_6$ in the flow interacting with surface and in unperturbed flow, and the enrichment factor in  $SF_4$  in the <sup>34</sup>S isotope. Fig. 4 shows the frequency dependencies (the spectra) of the HF\* fluorescence intensity in the case of excitation of  $SF_6$  in the mixture with  $H_2$  (SF<sub>6</sub>/H<sub>2</sub> = 1/1) in unperturbed flow (curve 1), in the flow incident on the surface (curve 2), and in the shock wave (curve 3). The total pressure of the gas above the nozzle was 2.4 atm. The exciting energy fluence was  $\Phi_{av} \cong 5 \text{ J/cm}^2$ . The distance from the nozzle to the surface was 51 mm,  $\Delta x = 2.5$ mm. The spectra are normalized in maxima. The fluorescence intensities in maxima of these HF \* spectra are related as  $I_1/I_2/I_3 = 1:5.2:19.5$ . One can see that, although the width of the HF\* fluorescence intensity spectrum in the shock wave is much broader than in unperturbed flow, the ratios of intensities of the HF\* fluorescence in maxima and in long wavelength wings of the spectra (near the  ${}^{34}SF_6\nu_3$  absorption band,  $\approx 930.5 \text{ cm}^{-1}$  [19]) do not differ strongly



Fig. 4. The frequency dependencies (the spectra) of the HF \*-fluorescence intensity in the case of excitation of SF<sub>6</sub> in the mixture with H<sub>2</sub> (SF<sub>6</sub> /H<sub>2</sub> = 1/1) in unperturbed flow (curve 1), in the flow incident on the surface (curve 2), and in the shock wave (curve 3). The spectra are normalized in maxima. The intensities of the spectra in maxima are related as:  $I_1 / I_2 / I_3 = 1:5.2:19.5$ . For further details, see the text.

indicating comparable selectivities of  $SF_6$  dissociation in unperturbed flow and in the shock wave.

When measuring the enrichment factor in  $SF_4$  in the  ${}^{34}S$  isotope the SF<sub>6</sub> molecules were excited at the frequency of 929 cm<sup>-1</sup> (10P(36) CO<sub>2</sub> laser line), which is in resonance with the  $\nu_3$  vibration of the  $^{34}$ SF<sub>6</sub> [19]. The results of study of the yield of SF<sub>4</sub> product and the enrichment factor in it in the <sup>34</sup>S isotope under excitation of SF<sub>6</sub> in unperturbed flow and in the flow interacting with surface are summarized in Table 1. In the case of excitation of molecules in an unperturbed flow at energy fluence  $\Phi_{av} \cong 10$  $J/cm^2$ , the enrichment factor was equal to  $K_{34}^{prod} =$  $17 \pm 5$ , and in the case of excitation of SF<sub>6</sub> in the shock wave it was equal to  $K_{34}^{\text{prod}} = 14 \pm 3$ . Thus, the yield of products in the shock wave more than an order of magnitude exceeds that in an unperturbed flow, while the selectivity is only insignificantly smaller.

The increase of the yield of products in the shock wave is connected with the increase of (i) the gas density, (ii) the rate of chemical reactions, and (iii) the dissociation yield of molecules due to (a) more effective excitation of them in the shock wave, and (b) collisional dissociation of molecules excited below the dissociation limit. Such molecules cannot dissociate in an unperturbed flow because of the deficit of collisions. Table 1

The results of study of the yield of  $SF_4$  product and the enrichment factor in it in the <sup>34</sup>S isotope in the case of excitation of  $SF_6$  in unpertubed flow, in the flow incident on the surface and in the shock wave

SF <sub>6</sub> pressure	CO <sub>2</sub> laser line	Energy fluence	SF <sub>4</sub> product yield			Enrichment factor in SF <sub>4</sub>		
above the nozzle			Unperturbed flow	Incident flow	Shock wave	Unperturbed flow	Incident flow	Shock wave
(atm)		$(J/cm^2)$	(arb. un.)	(arb. un.)	(arb. un.)	$(K_{34}^{\text{prod}})$	$(K_{34}^{\text{prod}})$	$(K_{34}^{\text{prod}})$
1.25	10P(16)	12	$1 \pm 0.2$	$2.5 \pm 0.5$	$12 \pm 3$			
1.25	10P(36)	10				$17 \pm 5$	$15 \pm 3$	$14 \pm 3$

The maximum increase of the gas density in the shock wave is determined by the relation [10-12]:

$$\rho_2 / \rho_1 = (\gamma + 1) / (\gamma - 1)$$
(2)

where  $\rho_1$  and  $\rho_2$  are the gas densities in the incident flow and in the shock wave accordingly, and  $\gamma = c_p/c_v$  is the ratio of heat capacities. For SF<sub>6</sub> $\gamma \approx 1.1$  [20], therefore  $\rho_2/\rho_1 \approx 21$ .

Note that the maximum density of the gas in the excitation region (at a distance  $\Delta x = 2.5$  mm from the surface) was not reached (at smaller values of  $\Delta x$  the HF<sup>\*</sup> fluorescence intensity was greater), and the ratio  $\rho_2/\rho_1$  in the excitation region was less than the limit value. Therefore, the increase of the SF<sub>4</sub> yield in the shock wave was connected not only with the increase of gas density, but also with other factors considered above.

A rather high selectivity in the shock wave is a consequence of that the vibrational temperature as well as the rotational one of molecules in the flow interacting with surface are still rather low.

In the gas dynamically cooled molecular flow, the following non-equilibrium conditions are usually realized [1]:

 $T_{1,\text{tr}} \leqslant T_{1,\text{rot}} \leqslant T_{1,\text{vib}}$  ( $T_{1,\text{tr}}$ ,  $T_{1,\text{rot}}$  and  $T_{1,\text{vib}}$  are the translational, the rotational and the vibrational temperatures of the molecules, respectively. In the shock wave formed under interaction of the pulsed gas dynamically cooled molecular flow with the surface, due to the difference in the translational, rotational and vibrational relaxation rates [21] the 'reverse' non-equilibrium conditions may be realized:  $T_{2,\text{tr}} \ge T_{2,\text{rot}} \ge T_{2,\text{vib}}$ . In addition, because of a rather slow vibrational to translational relaxation rate (for SF<sub>6</sub>  $p\tau_{V-T} \cong 150 \ \mu\text{s}$  Torr [22]) the vibrational temperature of molecules in the shock wave in the case of utilization of a pulsed rarefied gas flow may practically not differ from the vibrational tempera-

ture in the incident flow  $(T_{2,vib} \cong T_{1,vib})$ , whereas  $T_{2,tr} > T_{1,tr}$  and  $T_{2,rot} > T_{1,rot}$ .

The heating of the gas in the shock wave at the expense of stagnation can be estimated [12]:  $\Delta T =$  $v_0^2/2c_n$ , where  $v_0$  is the flow velocity and  $c_n$  is the heat capacity of the gas. Taking corresponding values for SF<sub>6</sub> ( $v_0 \approx 420$  m/s,  $c_n \approx 665$  J/kg K [20]) we will obtain  $\Delta T \cong 130$ K. If the translational temperature of SF<sub>6</sub> in the incident flow is  $T_{1,tr} \leq 40$ K [8], then in the shock wave it is  $T_{2 \text{ tr}} \leq 170$  K. The rotational temperature is probably close to the translational one, and the vibrational temperature  $T_{2,vib} \cong$  $T_{1 \text{ vib}} \leq 150 \text{ K}$  [8]. Therefore, if in forming of selectivity the vibrational temperature is a dominant factor, then the selectivity of dissociation of molecules in the shock wave should not differ strongly from that in unperturbed flow, what we observed in the present experiments. Note also, the decrease of the selectivity in the shock wave due to heating of the gas in some cases can be compensated by its increase connected with the increase of the concentration of irradiated molecules [23].

#### 4. Conclusions

The isotopically selective IR multiphoton dissociation of  $SF_6$  molecules in the non-equilibrium conditions of the cold shock wave formed under interaction of a pulsed gas dynamically cooled molecular flow with solid surface was studied for the first time. The HF \* fluorescence detection method was used to obtain the laser frequence and energy fluence dependencies of the dissociation yield of molecules in the shock wave and in unperturbed flow. The SF<sub>4</sub> product yield and the enrichment factor in SF<sub>4</sub> in the <sup>34</sup>S isotope were also studied in the case of excitation of  $SF_6$  in the shock wave and in unperturbed flow. The obtained results show that the efficiency of isotopically selective IR multiphoton dissociation of molecules in the pulsed gas dynamic flow can be essentially increased at the expense of formation of a shock wave under interaction of molecular flow with solid surface.

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