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## **Final Report**

*Summarizing all progress on the tasks outlined in the proposal*

Grant title: **Advanced all-gas chemical generation of atomic iodine for a COIL, and testing the COIL operation including this method of atomic iodine generation**

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**14. ABSTRACT**  
This report results from a contract tasking Academy of Sciences as follows: The Grantee will investigate advanced methods for chemical generation of atomic iodine for a Chemical Oxygen-Iodine Laser (COIL). The experimental investigation will be performed on a small-scale pilot device in the case of basic study of the kinetics of atomic iodine generation via chemically generated fluorine atoms, and directly in a modified COIL device via both Cl and F atoms. Experimental work will be supported with computational modelling of both reaction systems; a simplified 1-D modeling, and more sophisticated 3-D CFD model will be employed.

**15. SUBJECT TERMS**  
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## DECLARATION

- (1) **The Contractor, Institute of Physics of the Academy of Sciences of the Czech Republic, hereby declares that, to the best of its knowledge and believes, the technical data delivered herewith under Contract No. FA8655-03-1-3A63 is complete, accurate, and complies with all requirements of the contract.**
  
- (2) **I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this Contract.**

Date: 23 October 2004

Name and Title of Principal Investigator: Dr. Jarmila Kodymová

Name and Title of Authorized Official: Ing. Karel Jungwirth, DrSc.  
Director of Institute of Physics AS

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## Outline of planned tasks

- 1/ To investigate experimentally and theoretically by modelling the chemical generation of atomic iodine in the reaction system  $F_2 + NO \rightarrow F + NOF$  and  $F + HI \rightarrow I + HF$  with a goal to get more detailed information about feasibility of this way of I atom generation for a COIL operation;
- 2/ To elaborate a constructional modification of the 5-cm-gain-length COIL device for its operation with I atom generation via F atoms (injection of reactants  $F_2$ , NO, and HI);
- 3/ To continue in optimization of gain and chemical efficiency employing the reaction system via Cl atoms on the modified supersonic 5-cm-gain-length COIL.

### I. The investigation of atomic iodine generation via atomic fluorine

#### 1. Introduction

Experimental and theoretical results on this reaction system were partly presented in our previous EOARD reports - Final Report of the previous grant<sup>1</sup>, and interim Report 001<sup>2</sup> and 002<sup>3</sup> of this grant. The kinetic package of reactions given below (with relevant rate constants in  $cm^3 molecule^{-1} s^{-1}$  and  $cm^6 molecule^{-2} s^{-1}$ , respectively) has been involved in this study.

<i>F atom generation</i>	$F_2 + NO \rightarrow F + NOF$	$k_1 = 7 \times 10^{-13} \exp(-1150/T)$	(F-1)
<i>I atom generation</i>	$F + HI \rightarrow I + HF$ (HF*)	$k_2 = 1.512 \times 10^{-10} \exp(-5057.8/RT)$	(F-2)
<i>F atom loss</i>	$F + NO + N_2 \rightarrow NOF + N_2$	$k_3 = 1.1 \times 10^{-31}$	(F-3)
	$F + NO + NO \rightarrow NOF + NO$	$k_4 = 1.7 \times 10^{-31}$	(F-4)
	$F + I_2 \rightarrow IF + I$	$k_5 = 4.3 \times 10^{-10}$	(F-5)
<i>F atoms recombination</i>	$F + F + N_2 \rightarrow F_2 + N_2$	$k_6 = 1.02 \times 10^{-37} T^{1.5}$	(F-6)
<i>F wall recombination</i>	$F + F + wall \rightarrow F_2 + wall$	$\gamma_7 = 0.05$	(F-7)
<i>I atoms recombination</i>	$I + I + N_2 \rightarrow I_2 + N_2$	$k_8 = 6.15 \times 10^{-34} (T/298)^{0.07} \exp(7433/RT)$	(F-8)
	$I + I + I_2 \rightarrow I_2 + I_2$	$k_9 = 2.68 \times 10^{-31} (T/298)^{-3.06} \exp(6568/RT)$	(F-9)
	$I + I + HI \rightarrow I_2 + HI$	$k_{10} = 8.13 \times 10^{-32} (T/298)^{-3.5}$	(F-10)
<i>I atom loss</i>	$I + NO + N_2 \rightarrow INO + N_2$	$k_{11} = 1.8 \times 10^{-32} (T/298)^{-1}$	(F-11)
	$INO + I \rightarrow I_2 + NO$	$k_{12} = 1.66 \times 10^{-10}$	(F-12)
	$I + F_2 \rightarrow IF + F$	$k_{13} = 8.57 \times 10^{-13} \exp(-9500/RT)$	(F-13)
<i>I wall recombination</i>	$I + I + M \rightarrow I_2 + M$	$\gamma_{14} = 1.0$	(F-14)

A heat effect of individual reactions can be estimated from their reaction enthalpies that are listed in the interim report.<sup>3</sup>

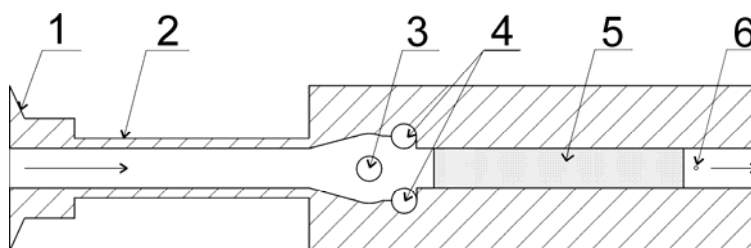
## 2. Investigations performed in the framework of this grant

In the interim Reports 001 and 002 of this grant<sup>2,3</sup>, we presented most of the experimental results obtained using diluted reacting gases (10% F<sub>2</sub>, 10% NO and 10% HI in N<sub>2</sub>) and at pressure up to 9 kPa (~ 67 torr). Our investigation was focused recently on atomic I generation

- i/ **employing higher flow rates** of these 10% reactants in order to prove feasibility of F and I atoms generation at higher pressure in the reactor, which would be desirable for the injection of atomic fluorine (or iodine) generated in a separate reactor into the primary gas flow with O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) in COIL (either upstream or downstream of the supersonic nozzle), and
- ii/ **employing more concentrated F<sub>2</sub> (20%) and non-diluted NO and HI** in order to reduce an effect of the ternary loss-reactions (F-3, 6, 7 and 10), and to increase also the gas temperature.

### 2.1. Experimental devices

Three types of experimental reactors were used for this investigation. A cross-section of the reactor with fixed injectors used as the first is shown in **Fig. 1**.

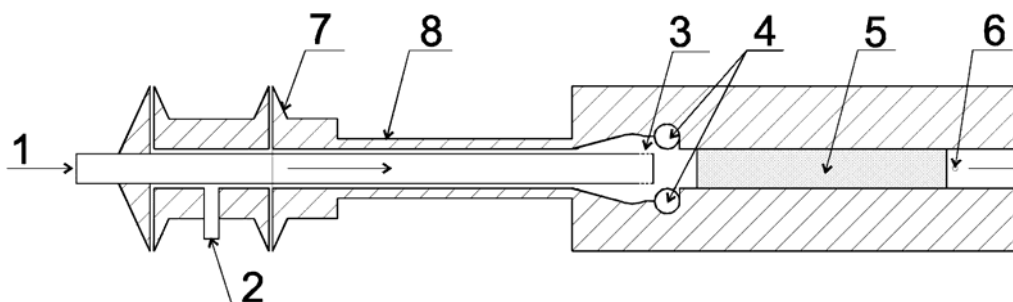


**Fig. 1.** Cross-section of transverse flow reactor with fixed injectors, 1 – input flange, 2 – delta-shaped channel, 3– NO injector, 4 – HI injectors, 5 – optical cavity for atomic I detection, 6 – thermocouple

The injector 3 placed in the center of the rectangular reactor cavity was used for injection of one of the secondary gases (10% NO or HI in nitrogen), and two injectors 4 for injection of the second of these gases. Two rows of 23 holes (in each row) of 0.4 mm i.d. and two rows of 22 holes of 0.3 mm i.d. (in each row) were drilled in the injector 3. A distance between nearby holes in one row was 1 mm. The 0.4 mm-holes were oriented in vertical direction (up and down), and the 0.3 mm-holes were turned by 30° to rows with 0.4 mm holes downstream of the primary flow with 10% F<sub>2</sub>. The tube injectors 4 with one row of 23 holes of 0.4 mm oriented perpendicularly to the primary flow,

and one row of 22 holes of 0.3 mm oriented by  $60^\circ$  to the primary flow were placed at the reactor wall. Two side windows of the reactor served for detection of atomic I and recording its concentration profile along the flow in the reactor. The probe beam of the Iodine Scan Diagnostics (further ISD) passed through these wedge-shaped windows perpendicularly to the gas flow. A velocity of the probe beam moving along the duct axis was  $4 \text{ mm s}^{-1}$ . The ISD probe beam emitter/detector unit was mounted on the assembly of motorized linear positioning equipment controlled by PC making possible to record atomic iodine signal on the path of 13 to 60 mm distant from the axis of the injectors 4 (dotted area in Fig. 1). This path corresponded to a time interval of 0.45 - 2 ms between injection of the gas by the injector 4 and I detection (a rotary pump of  $30 \text{ m}^3 \text{ h}^{-1}$  was used and gas temperature of 400 K was considered). Gas temperature was measured by a jacketed Ni-CrNi thermocouple 6 (1 mm o.d.) inserted perpendicularly to the gas flow at 5 mm downstream of the windows end.

A cross-section of the reactor with a movable injector is shown in **Fig. 2**.

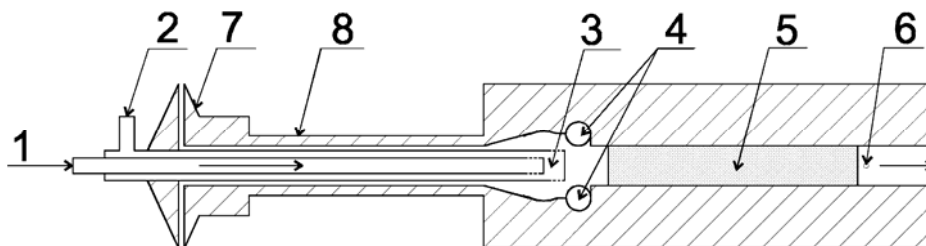


**Fig. 2.** Scheme of atomic iodine reactor with movable NO injector  
 1 - NO inlet, 2 –  $\text{F}_2 + \text{N}_2$  mixture inlet, 3 – generation region of F atoms,  
 4 – HI injectors, 5 – optical cavity for atomic I detection, 6 – thermocouple,  
 7 – input flange, 8 – delta-shaped channel

The reactor with axially movable NO injector 1 made possible to vary a time delay between NO and HI injection. The injector 1 was formed by a stainless steel tube of 6 mm i.d. with 24 holes (1.1 mm i.d.) drilled along the tube perimeter in three rows (1.5 mm between each row). This injector was inserted into a delta-shaped entrance space of the reactor body. The 10%  $\text{F}_2/\text{N}_2$  mixture was introduced through the inlet 2. The 9.6 %  $\text{HI}/\text{N}_2$  mixture was injected through two injectors 4.

A cross-section of the third reactor is shown in **Fig. 3**. This reactor was used mainly for investigations with more concentrated gases (20 %  $\text{F}_2/\text{N}_2$ , and non-diluted NO and HI). Atomic F was generated in the space of the inner coaxial reactor 3 with the tube 2 for  $\text{F}_2$  inlet and the tube for NO inlet 1 (2 mm i.d.) This coaxial reactor was inserted into a delta-shaped entrance space of the

main reactor. Non-diluted NO was injected into the  $F_2/N_2$  flow through 6 holes (0.3 mm i.d.) drilled in one row along the perimeter of the tube **1**. The gas with generated F atoms exited the reactor **3** through 24 holes (1.1 mm i.d.) drilled along the perimeter of its outer tube in three rows of 1.5 mm distant from each other.



**Fig. 3.** Scheme of atomic iodine reactor with embedded reactor for generation of F atoms  
**1** – NO inlet, **2** –  $F_2/N_2$  inlet, **3** – generator of F atoms, **4** – HI injectors,  
**5** – optical cavity for ISD detection, **6** – thermocouple, **7** – input flange,  
**8** – delta-shaped channel

This reactor was used also for estimation of the wall recombination of generated atomic iodine. For this purpose, a fine stainless steel mesh was inserted perpendicularly across the overall gas flow through the cavity (nearly at the center of the probe beam path). The mesh with 0.2 mm openings was made of wire of 0.11 mm thick.

## 2.2. Experimental Results

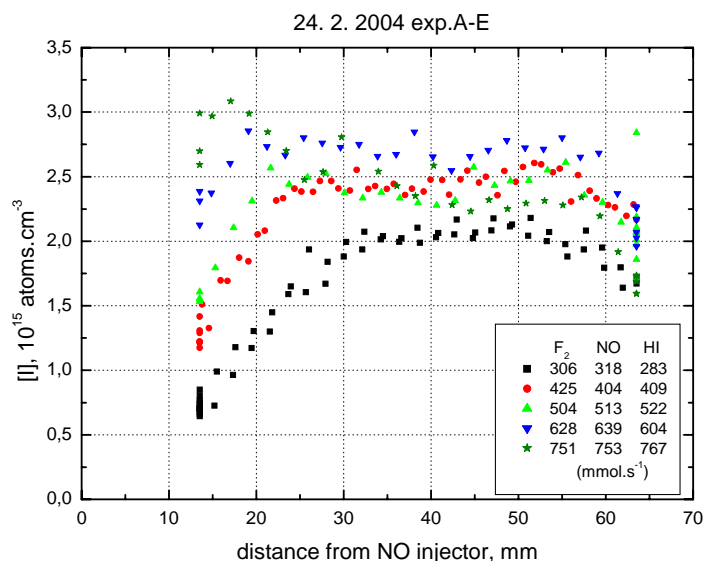
In this chapter are summarized the main results obtained during the first half of this grant period (given in more detail in the interim Report<sup>2,3</sup>) and comprehensive results gathered recently.

### 2.2.1. Results on the reactor with fixed injectors, HI–NO injection order, all reactants diluted with nitrogen (10% mixtures), higher flow rates of reactants

**Fig. 4** shows the effect of  $F_2$ , NO and HI flow rate (in equimolar ratio approximately (1:1:1)) on atomic iodine concentration recorded in the optical cavity along the gas flow. These measurements showed that I concentration increased with increasing flow rates of reactants, and a maximum of the curves was shifted in the upstream direction. This indicates that both the production and loss-reactions are accelerated with increasing partial pressure of reacting gases. At higher flow rates (and higher pressure), the yield of atomic iodine (i.e. the ratio of I flow / input  $F_2$



flow) was lower obviously due to an increasing effect of ternary loss reactions of atomic F (F-3, 4), and atomic I (F-8 – 11, 14).

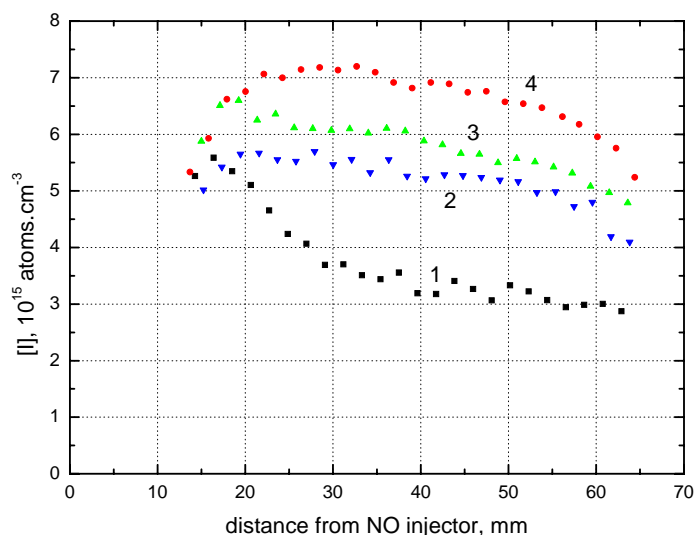


**Fig. 4.** Atomic iodine concentration recorded along gas flow at different flow rates of reactants and HI:NO:F<sub>2</sub> = 1:1:1 approx.  
P = 2.9 – 7.3 kPa (22 – 55 torr),  $\tau_{\text{HI-NO}} = 0.18$  ms,  $\tau_{\text{NO-ISD}} = 0.45$ -2 ms

An example of the dependence of atomic I concentration recorded along the flow on the HI flow rate at NO/F<sub>2</sub>  $\cong$  1 is shown in **Fig. 5**. At the lowest HI flow rate (curve 1), the atomic I concentration was decreasing rapidly with a distance from the NO injection obviously due to the consumption of I atoms in the reaction with F<sub>2</sub> (F-13). At higher HI flow rates (curves 2, 3, 4), this effect was partly compensated by the reaction of F atoms formed in the reaction (F-13) with HI, producing additional I atoms. The same effect was observed also in the range of higher pressure of 7.4 – 9.2 kPa (55 – 69 torr). We observed also in this pressure range that atomic I concentration did not increase already with increasing HI flow rate and even declined, owing to increasing effect of the excessive nitrogen and HI in HI/N<sub>2</sub> mixture on the rate of ternary loss reactions for F atoms (F-3, 4), and I atoms (F-8, 10 and 11).

Study of the effect of excessive NO against F<sub>2</sub> on atomic I generation at higher pressure (3.7 – 5.5 kPa) showed that the I concentration was not diminished by the termolecular loss-reactions (F-3, 4) up to 50% excess of NO. A maximum flow rate of atomic iodine that we obtained in these experiments was 180  $\mu\text{mol/s}$  and the I yield ranged from 9 to 27 % related to F<sub>2</sub>, and from 25 to

42 % related to HI. The HI-NO injection order provided better results than NO-HI order due to a lower loss of F atoms (more detailed explanation can be found in the interim reports<sup>2,3</sup>).

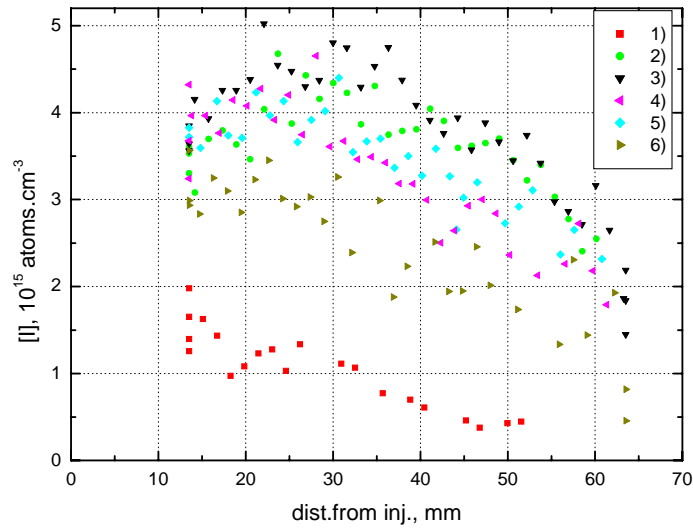


**Fig. 5.** Atomic iodine concentration recorded along gas flow at different HI flow rate (in  $\mu\text{mol/s}$ ): 1 – 291, 2 – 394, 3 – 409, 4 – 453; 583  $\mu\text{mol/s}$   $\text{F}_2$ , 582  $\mu\text{mol/s}$   $\text{NO}$ ,  $P = 5.5 - 6$  kPa,  $\tau_{\text{HI-NO}} = 0.18$  ms,  $\tau_{\text{NO-ISD}} = 0.45-2$  ms

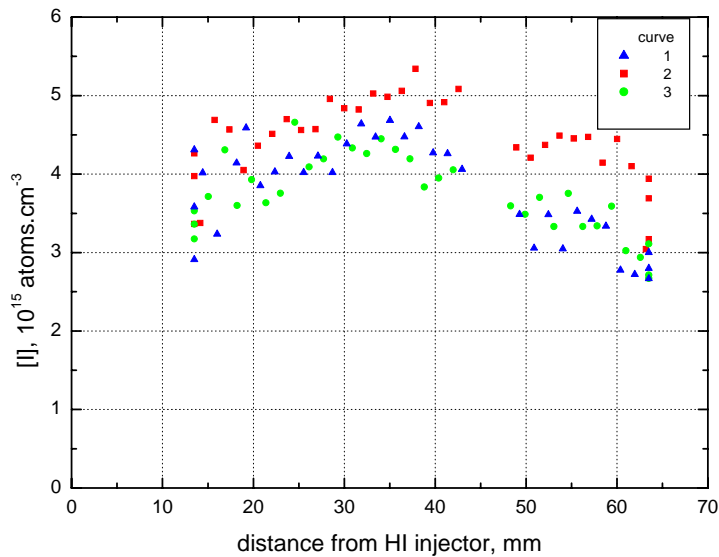
### 2.2.2. Results on the reactor with movable NO injector and with 10% mixtures of all reactants with nitrogen

**Fig. 6** shows a course of atomic I concentration along the gas flow in dependence on HI flow rate and at a time interval of 0.64 ms between NO and HI injection. The initial increase in I concentration with increasing HI flow rate follows from the first order of reaction (F-2) with respect to HI. The following decrease may be explained by an increasing effect of excessive  $\text{N}_2$  and HI in HI/ $\text{N}_2$  mixture on the rate of the ternary loss-reactions of F atoms (F-3, 4), and I atoms (F-8 – 11).

Similar dependences as in Fig. 6 were measured with prolonging the interval between NO and HI injection by 25% (a time delay of 0.8 ms). It had no distinct effect on I production, which can be seen also in **Fig. 7** showing the I concentration profiles for different NO-HI time intervals. These results proved a rather long lifetime of F atoms under these conditions. This fact was revealed by modeling of this reaction system (it can be seen in **Fig. 23** in interim Report 002).



**Fig. 6.** Atomic iodine concentration along gas flow at different HI flow rate (in  $\mu\text{mol/s}$ ): 1 – 123, 2 – 250, 3 – 331, 4 – 398, 5 – 459, 6 – 605; 791  $\mu\text{mol/s}$   $\text{F}_2$  and 736  $\mu\text{mol/s}$   $\text{NO}$ ;  $P = 5.6 - 13$  kPa (42 – 97.5 torr),  $\tau_{\text{NO-HI}} = 0.64$  ms,  $\tau_{\text{HI-ISD}} = 0.45 - 2$  ms



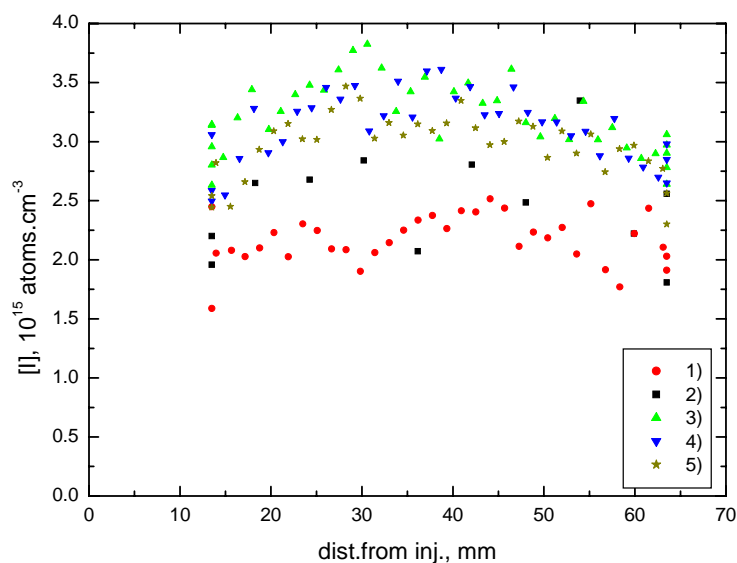
**Fig. 7.** Atomic iodine concentration along gas flow at different time interval between  $\text{NO}$  and  $\text{HI}$  injection,  $\tau_{\text{NO-HI}}$  (ms): 1 – 0.64, 2 – 0.8, 3 – 1.015; 608  $\mu\text{mol/s}$   $\text{F}_2$ , 642  $\mu\text{mol/s}$   $\text{NO}$ , and 502  $\mu\text{mol/s}$   $\text{HI}$ ,  $P = 7.6 - 9$  kPa (57 – 67 torr),  $\tau_{\text{HI-ISD}} = 0.45 - 2$  ms

In this experimental arrangement and at pressure above 5 kPa, the yield of atomic iodine ranged from 3 to 13 % only (related to  $\text{F}_2$  flow), and from 8 to 35 % (related to  $\text{HI}$ ).

2.2.3. Results on the reactor for F generation embedded into the reactor for I generation, NO-HI injection order, 10% F<sub>2</sub>/N<sub>2</sub> and HI/N<sub>2</sub>, and non-diluted NO

This study was performed on the device in Fig. 3 designed for generation of F atoms at higher temperature and pressure in the reactor that was separated from the reactor for atomic I generation. Non-diluted NO was used with the aim: (i) to reduce the undesirable effect of an excessive N<sub>2</sub> diluent on the rate of ternary loss-reactions (F-3, 8 and 11), and (ii) to elevate temperature and so increase the rate constants of production reactions (F-1 and 2), and to decrease the rate constants of the loss-reactions (F-3, 8-11).

The course of I concentration along the reactor for this configuration and conditions and at different HI flow rates is shown in **Fig. 8**.

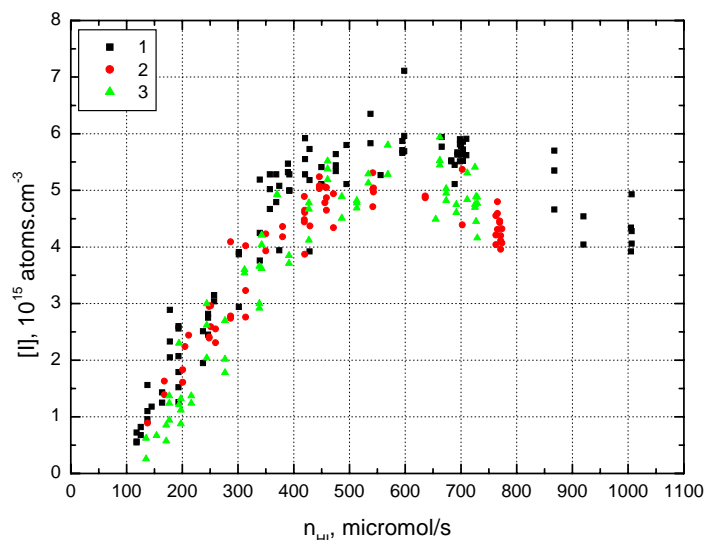


**Fig. 8.** Atomic iodine concentration along gas flow at different HI flow rate ( $\mu\text{mol/s}$ ):  
 1 – 172, 2 – 188, 3 – 292, 4 – 294, 5 – 333;  
 459  $\mu\text{mol/s}$  F<sub>2</sub> and 433  $\mu\text{mol/s}$  NO;  $\tau_{\text{NO-HI}} = 0.8$  ms,  $\tau_{\text{HI-ISD}} = 0.45 - 2$  ms

The estimated pressure in the inner reactor for F atoms generation was 6.6 – 8.1 kPa (50 – 61 torr), while the pressure in the reactor (in detection cell) where atomic I was generated was 3.3 – 3.9 kPa (25 – 29 torr). A time interval between NO-F<sub>2</sub> mixing and the gas exit from the F-reactor was 14  $\mu\text{s}$  and the interval between exit of F atoms and HI admixing was 1.1 ms. The results in Fig. 8 show that maximum I concentration was obtained at a medium HI flow rate (292 - 294  $\mu\text{mol/s}$ ). Further HI flow rate increase did not lead to an increase in atomic I concentration. The reason was

obviously due to an acceleration of the reaction (F-10) due to a higher partial pressure of  $N_2$  and HI in the HI/ $N_2$  mixture.

A change of the time interval between NO injection and exit from F reactor,  $\tau_{NO-F}$ , within 0.014 - 0.24 ms had no significant effect on atomic iodine production. It can be seen in **Fig. 9** that shows dependence of I concentration on HI flow rate for the different intervals. This agrees also with modeling results of the system for these conditions (calculated pressure in the F reactor was 7 – 12.5 kPa).



**Fig. 9.** Atomic I concentration in dependence on HI flow rate at different intervals between NO and F injection,  $\tau_{NO-F}$  (ms): 1 – 0.014, 2 – 0.09 ms, 3 – 0.24 ms; 794  $\mu\text{mol/s}$   $F_2$  and 718  $\mu\text{mol/s}$  NO

A decrease in I concentration at HI flow rates above  $\sim 600 \mu\text{mol/s}$  was caused probably by increasing loss of I atoms in reactions (F-8, 10 and 11).

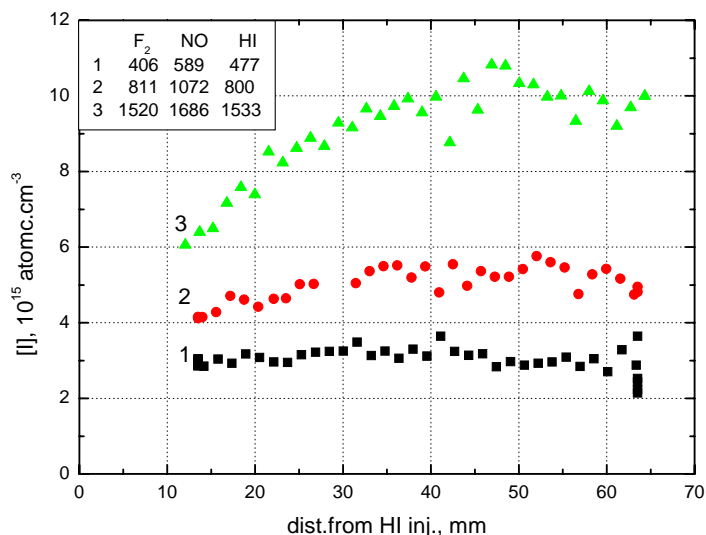
The yield of atomic iodine in these measurements with non-diluted NO was 8 – 17 % related to  $F_2$ , and 11 – 37 % related to HI, which is slightly higher than results obtained with 10 % NO (the chapter 2.3.2.). It is probably a consequence of a lower rate of the loss-reactions (F-3, 4 and 8-11) and higher gas temperature in the F reactor (by 50 – 100 K), which is favorable for F production.

#### 2.2.4. Results on the reactor for F generation embedded into the reactor for I generation, NO-HI injection order, 20% $F_2/N_2$ mixture, and non-diluted NO and HI

In this set of experiments, 20%  $F_2/N_2$  mixture instead of 10% mixture, and non-diluted NO and HI instead of 10% mixtures were used, in order to suppress the loss-ternary reactions including  $N_2$ ,

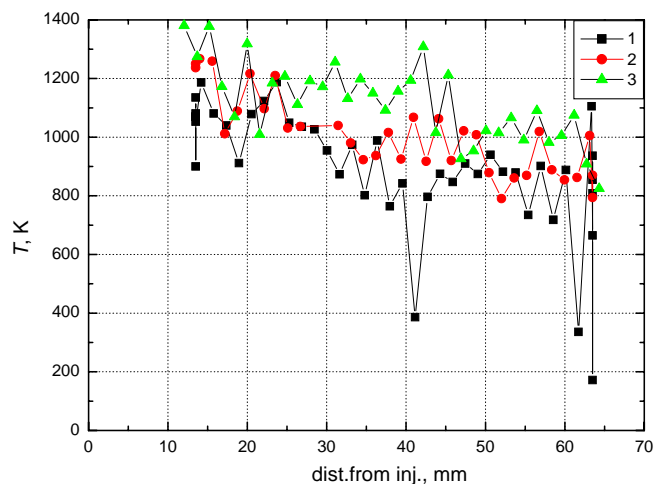
and to increase the gas temperature. Modeling results predicted a positive effect of both (see chapter 2.3.2).

The first series of experiments was performed with NO introduced through the inner injector (labeled **1** in Fig. 3), F<sub>2</sub>/N<sub>2</sub> mixture through inlet **2**, and concentrated HI through two injectors **4**. **Fig. 10** shows an example of obtained dependence of atomic I concentration on the flow rate of all three reactants (at the ratio 1 : (1.1÷1.4) : 1).



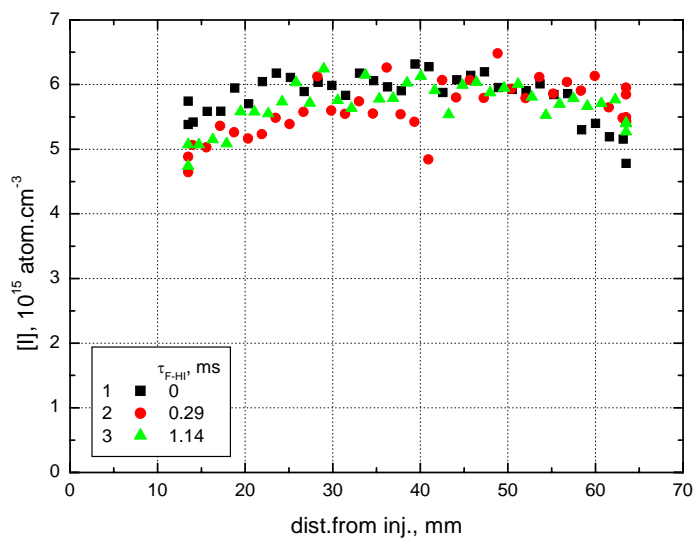
**Fig. 10.** Effect of F<sub>2</sub>, NO, and HI flow rate (in μmol/s) on I concentration,  $\tau_{\text{NO-F}} = 0.01$  ms,  $\tau_{\text{F-HI}} = 0.29$  ms,  $P_{\text{F}} = 4.4 - 17.3$  kPa (33 - 130 torr),  $P_{\text{I}} = 1 - 3$  kPa (7.5 - 22.5 torr)

A comparing the curve 1 and 2 indicates that a twofold increase in flow rates of all reactants resulted in approx. 1.7times higher I concentration. The production rate of I atoms increased even more (approx. twice) due to a higher gas temperature (see **Fig. 11**), and so a higher volumetric gas flow rate in the detection cell. Another twofold increase in the reactant flow rates caused also another increasing in I concentration nearly twice (curve 3 in Fig. 11), and the I flow rate still more. It means that, in contrary to the experiments with 10 % reactants, a higher gas pressure did not caused a decrease in the yield of atomic iodine.



**Fig. 11.** Effect of  $F_2$ , NO, and HI flow rate on gas temperature, labeling and conditions as in Fig. 10.

The rate of atomic I production and the gas temperature were not significantly influenced by increasing the time interval between gas exit from the F-reactor and HI injection ( $\tau_{F-HI}$ ) (**Fig. 12**).

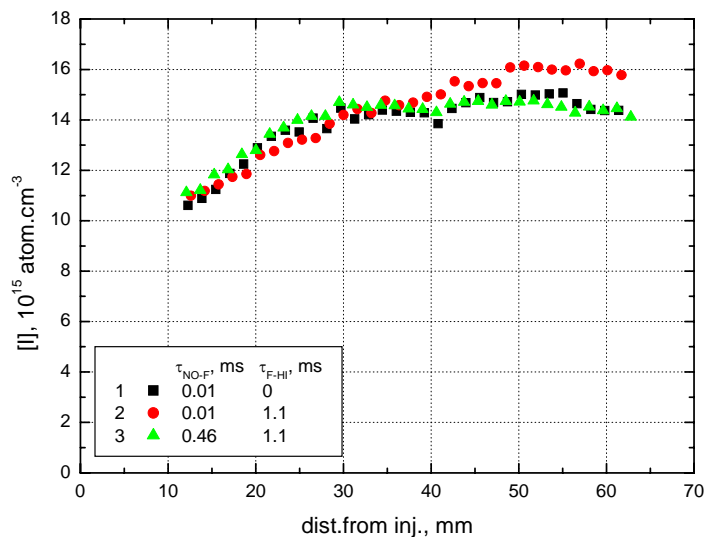


**Fig. 12.** Effect of time interval between gas exit from F reactor and HI injection (ms): 1 – 0, 2 – 0.29, 3 – 1.14; 0.81 mmol/s  $F_2$ , 1.04 mmol/s NO, 0.8 mmol/s HI,  $\tau_{NO-F} = 0.16$  ms,  $P_F = 8.5$  kPa (64 torr),  $P_I = 1.8$  kPa (13.5 torr)

Also a change of the time interval between NO/ $F_2$  mixing and gas exit from F reactor,  $\tau_{NO-F}$ , within 0.01 – 0.16 ms did not affect atomic I production.

Similar measurements were performed with higher flow rates of reactants. The former HI injectors were replaced with modified injectors with one row of 19 holes of 0.6 mm i.d. for attaining

a higher HI penetration. **Fig. 13** shows that I concentration was substantially increased, but the different time intervals  $\tau_{\text{NO-F}}$  and  $\tau_{\text{F-HI}}$  had no effect in these conditions (pressure in the inner F reactor,  $P_{\text{F}} \sim 20$  kPa (150 torr), pressure in the I reactor,  $P_{\text{I}} \sim 4.5$  kPa (34 torr)).



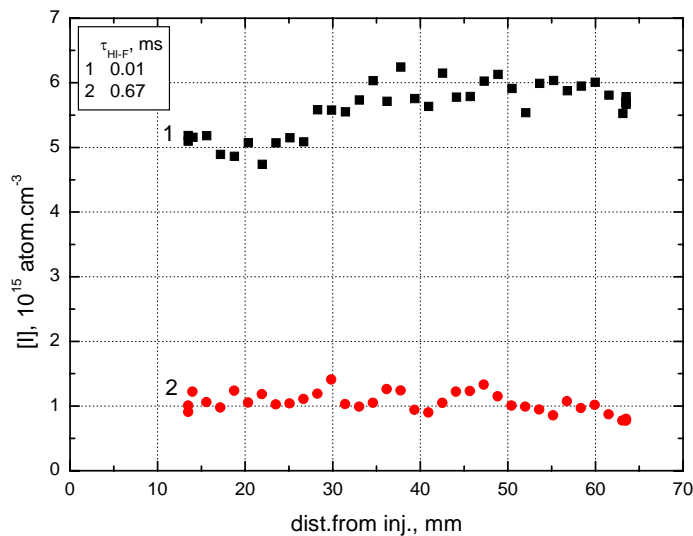
**Fig. 13.** Atomic iodine concentration along gas flow at different intervals between NO injection and gas exit from the F reactor,  $\tau_{\text{NO-F}}$ , and between F reactor exit and HI injection,  $\tau_{\text{F-HI}}$ ; 1.52 mmol/s  $\text{F}_2$ , 1.64 mmol/s NO, 2.16 mmol/s HI,  $P_{\text{F}} = 20$  kPa,  $P_{\text{I}} = 4.5$  kPa

The results in Figs. 12 and 13 demonstrate a high stability of F atoms in this reaction system even at rather high pressure (20 kPa (150 torr)). This is in agreement with the modeling results. A yield of atomic iodine was higher in these experimental conditions, 26 – 47 % (related to  $\text{F}_2$ ) and 27 – 37 % (related to HI). It is obviously due to lower rates of the loss-reactions (F-3, 4 and 8-11), and higher gas temperature owing to a lower partial pressure of  $\text{N}_2$  diluent.

Further set of experiments served for an estimation of the rate constant of  $\text{F}_2 + \text{HI}$  reaction that was not found in literature. In this measurement, HI was introduced through the inner injector (labeled 1 in Fig. 3),  $\text{F}_2/\text{N}_2$  mixture through the inlet 2, and non-diluted NO through the injectors 4. **Fig. 14** illustrates that a premixing time of  $\text{F}_2$  with HI had a strong effect on I production. If this time was prolonged from 0.01 ms to 0.16 ms, the rate of I production decreased 7.4times. It indicates a fast rate of the reaction

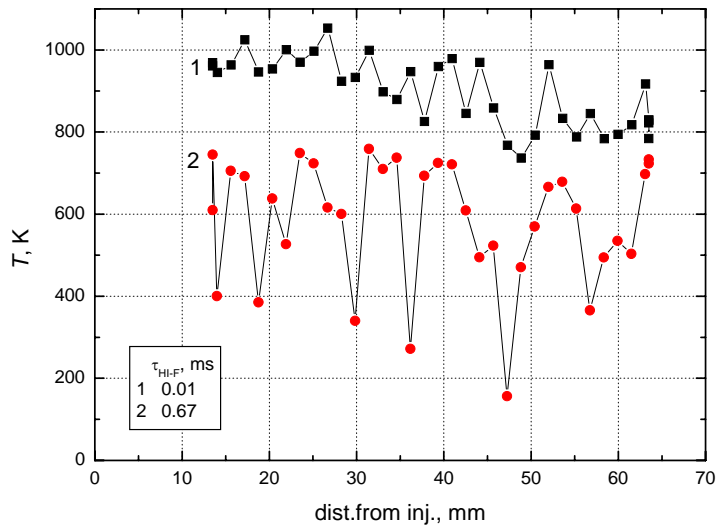






**Fig. 14.** Effect of mixing time of F<sub>2</sub> + HI on I production;  
0.78 mmol/s F<sub>2</sub>, 1.1 mmol/s NO, 0.86 mmol/s HI

The gas temperature in the detection cell was rather lower (670 K in average) in the measurement when the time interval of mixing was longer, and much larger scattering of T values was observed (curve 2 in **Fig. 15**). We based an estimation of the rate constant of reaction (F-15) on the assumption that both F<sub>2</sub> and HI concentrations before NO admixing were 2.72 times ( $=\sqrt{7.4}$ ) lower in the experiment with a longer time interval. A calculated rough estimate of this rate constant was then  $1.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ . This value is by an order of magnitude higher than the value given in our interim Report 002<sup>3</sup> ( $1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ). That value was estimated from I<sub>2</sub> concentration calculated from measured light absorption (at 488 nm), assuming that I<sub>2</sub> is the only product of the reaction (F-15). This assumption could be incorrect because other reaction products like some inter-halogen compounds (IF<sub>x</sub>) may be formed by this reaction. Moreover, the earlier measurements were performed at much lower gas temperature and pressure ( $\sim 320 \text{ K}$  and  $0.9 \text{ kPa}$ ) than the new value ( $\sim 715 \text{ K}$  and  $8.5 \text{ kPa}$ ).



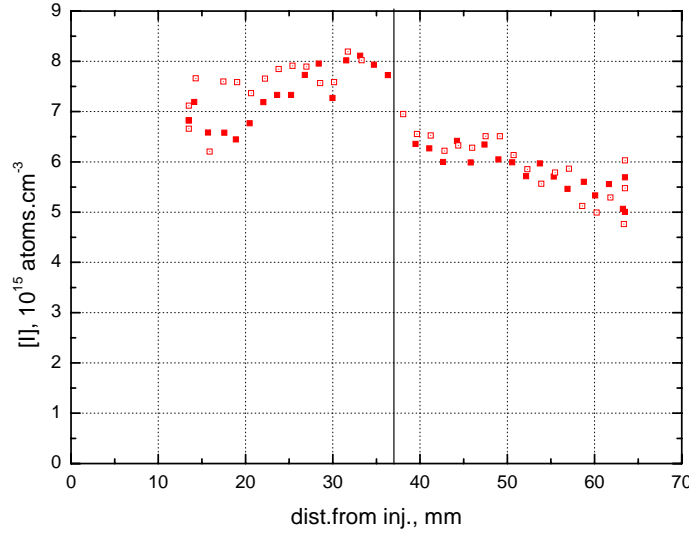
**Fig. 15.** Effect of time interval between the HI + F<sub>2</sub> mixing and gas exit from inner reactor on gas temperature; 785 F<sub>2</sub> + 1100 NO + 858 HI

#### 2.2.5. Experimental estimation of atomic iodine loss by the wall recombination

The wall recombination of atomic iodine was roughly estimated from its loss on a fine stainless steel mesh placed across the optical cavity in the rectangular reactor perpendicularly to the gas flow. A concentration of atomic I was measured upstream and downstream of the mesh that was distant by 37 mm from the HI injection. A drop in I concentration on the mesh was 10 – 20 % (evaluated from 4 measurements). An example of the measured I concentration profile is shown in **Fig. 16**. Calculations presented in the interim report<sup>3</sup> showed that the wall recombination of I atoms on the mesh surface was controlled by diffusion. This result was used also for calculation of the fraction of F atoms recombined on the walls of inner coaxial 25 mm long reactor at pressure 11.3 kPa (85 torr) and temperature 477 K. The estimated fraction of F atoms recombined on the reactor walls and during gas exit from the reactor is 4.1 % and 3.2 %, respectively, of the total produced F atoms.

#### 2.2.6. Temperature of reaction mixture

The gas temperature attained at most ~ 700 K in experiments with 10 % reactants/N<sub>2</sub> mixtures, and up to 1000 – 1200 K with 20 % F<sub>2</sub>/N<sub>2</sub> mixture, and non-diluted NO and HI. These results are in agreement with calculations given in the interim report<sup>2</sup>.



**Fig. 16.** Estimation of atomic I wall recombination; I concentration measured before and after gas passing through the fine stainless steel mesh  
0.8 mmol/s F<sub>2</sub>, 0.89 mmol/s NO, 0.64 – 0.58 mmol/s HI

### 2.3. Theoretical estimations and modeling results

#### List of symbols

$A_h$ ... channel cross-section	$Q$ ... reaction heat
$A$ ... corrected cross-section	$Re$ ... Reynolds number of the mixture
$A^*$ ... cross section occupied by effective boundary layer	$T$ ... static temperature of mixture
$c_{psi}$ ... specific heat capacity of i-th gas	$T_{0i}$ ... total temperature of i-th gas
$D_i$ ... diffusion coefficient of i-th species	$u$ ... gas velocity
$h_i$ ... molar enthalpy of formation of the i-th species	$W$ ... molar weight of the mixture
$k_j$ ... rate constant of the j-th reaction	$W_i$ ... molar weight of the i-th species
$l_m$ ... minimum distance to wall	$w_i$ ... mass fraction of i-th species
$\dot{m}$ ... mass flowrate of mixture	$x$ ... downstream distance
$\dot{m}_i$ ... mass flowrate of i-th gas	$\alpha_{ji}$ ... reaction order of i-species in j-th reaction

$\dot{n}$ ... molar flowrate of mixture	$\delta^*$ ... displacement thickness (effective b.l. thickness)
$\dot{n}_i$ ... molar flowrate of i-th gas	$\rho$ ... density of mixture
$p$ ... static pressure	$\nu_{ji}$ ... stoichiometric coefficient of i-species in j-th reaction

### 2.3.1. Progress in mathematical modeling

A new quasi one-dimensional kinetic model was developed during the period of this grant solution. It takes into account all-important multidimensional features: a convective-diffusive mixing of reactants, area change and boundary layer. It is applicable for both subsonic and supersonic flow. The model using a subsequent admixing of gases 2 and 3 into gas 1 and consists of this set of equations:

$$dp + \rho u du + \rho u^2 \frac{d\dot{m}}{\dot{m}} = 0 \quad (\text{M-1})$$

$$\frac{d\dot{m}_2}{\dot{m}} c_{ps2} T_{02} + \frac{d\dot{m}_3}{\dot{m}} c_{ps3} T_{03} = dQ_r + T \left( \frac{d\dot{m}}{\dot{m}} c_{ps} + \frac{dc_{ps}}{c_{ps}} \right) + c_{ps} dT + \frac{1}{2} \frac{d\dot{m}}{\dot{m}} u^2 + u du \quad (\text{M-2})$$

$$d\rho u A + \rho du A + \rho dA u = d\dot{m} \quad (\text{M-3})$$

$$d\rho = \frac{1}{RT^2} (dpTW + p dWT - dTpW) \quad (\text{M-4})$$

$$dw_i = \frac{W_i}{N_A \rho u} \sum_{j=1}^R \nu_{ji} k_j (N_A \rho)^{\sum_{k=1}^N \alpha_k} \prod_{k=1}^N \left( \frac{W_k}{W_k} \right)^{\alpha_k} \quad (\text{M-5})$$

$$A = A_h - A^* (\delta^*) \quad (\text{M-6})$$

$$\dot{m} = \dot{m}_1 + \dot{m}_2 (1 - \varphi_2(x)) + \dot{m}_3 (1 - \varphi_3(x)) \quad (\text{M-7})$$

$$\dot{n} = \dot{n}_1 + \dot{n}_2 (1 - \varphi_2(x)) + \dot{n}_3 (1 - \varphi_3(x)) \quad (\text{M-8})$$

$$c_{ps} = \frac{\dot{m}_1}{\dot{m}} c_{ps1} + \frac{\dot{m}_2}{\dot{m}} c_{ps2} \left( 1 - \varphi_2(x) \right) + \frac{\dot{m}_3}{\dot{m}} c_{ps3} (1 - \varphi_3(x)) \quad (\text{M-9})$$

$$W = \frac{\dot{m}}{\dot{n}} \quad (\text{M-10})$$

$$\varphi_2(x) = \exp\left(-\frac{k_{m2}}{u} x\right) \quad (\text{M-11})$$

$$\varphi_3(x) = \exp\left(-\frac{k_{m3}}{u} x\right) \quad (\text{M-12})$$

$$dQ = \sum_i \frac{h_i}{W_i} dw_i \quad (\text{M-13})$$

$$\delta^* = 1.73 \sqrt{\frac{x}{\text{Re}}} \quad (\text{M-14})$$

The kinetic model includes the package of all reactions (F-1-14) with their rate constants.

The finite mixing of reactants of gases 2 and 3 is incorporated into the chemical term (M-5) by using dummy first-order reactions



where  $k_{m2}, k_{m3}$  are parameters.

These parameters can be adjusted according to 3-D modeling results or experimental results, and are used also for modeling of an influence of the finite mixing on the flow properties by means of the definitions (M-11) and (M-12).

The present quasi-1-D model was used for explaining the experimental results on atomic iodine generation via fluorine atoms on the small-scale apparatus and optimization of its performance. A very good agreement between modeling and experimental results was achieved for selected experiments, after adjusting the mixing rate of HI. More details were given in the interim report<sup>3</sup>, where the effect of heterogeneous recombination of iodine atoms was investigated experimentally. A new effective rate constant for the recombination of atoms on the walls of reactor was derived in dependence on the diffusion coefficient and flow tube (reactor) dimensions:

$$1/k_{het} = 1/k_{wall} + 1/k_{diff}, \quad (\text{M-17})$$

where

$$k_{wall} = \gamma_i \frac{A}{V} \sqrt{\frac{RT_{wall}}{2\pi W_i}} \quad (\text{M-18})$$

$$k_{diff} = a \frac{D_i}{l_m^2}, \quad (\text{M-19})$$

$a$  is a parameter,  $i = \text{F or I species}$ , and the diffusion coefficient is dependent on the pressure and temperature.

Using the derived effective recombination constants, the 7 % loss of F atoms in the coaxial reactor was estimated. When heterogeneous recombination of iodine atoms was incorporated into the quasi-1-D model, the rate atomic I production was by about 15 – 30 % lower then with no wall deactivation.

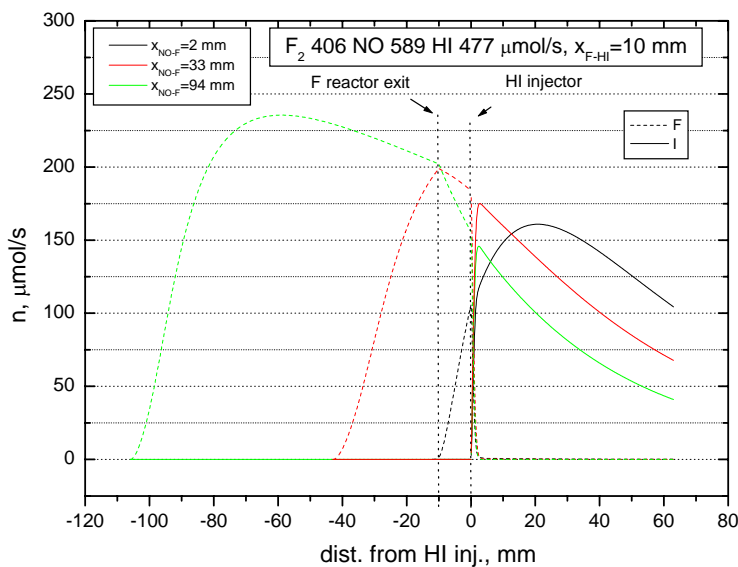
### 2.3.2. Estimation of F generation under higher pressure and temperature

A detailed analysis of the effect of pressure and temperature on atomic F and atomic I production was presented in the interim report.<sup>2</sup> It was calculated that NOF (the product of the loss reaction (2)) is thermodynamically stable up to very high temperature (the dissociation fraction of 0.5 is attained at 1800 K only). On the other hand, the 1-D modeling of the reaction kinetics has shown that a rather high yield of F atoms (over 50 %) may be attained at much lower temperature (over 700 K) when 20 % F<sub>2</sub>/N<sub>2</sub> mixture and non-diluted NO is used. These modeling results were fully verified by experimental results given the chapter 2.3.4.

### 2.3.3. Estimation of effect of time intervals between gases injection

An effect of the distance (time interval) between NO injection and the gas exit from the coaxial F reactor was modeled for 10% F<sub>2</sub>/N<sub>2</sub> mixture. The results were published in the interim report<sup>3</sup>, showing a small decrease in I production rate with increasing this distance.

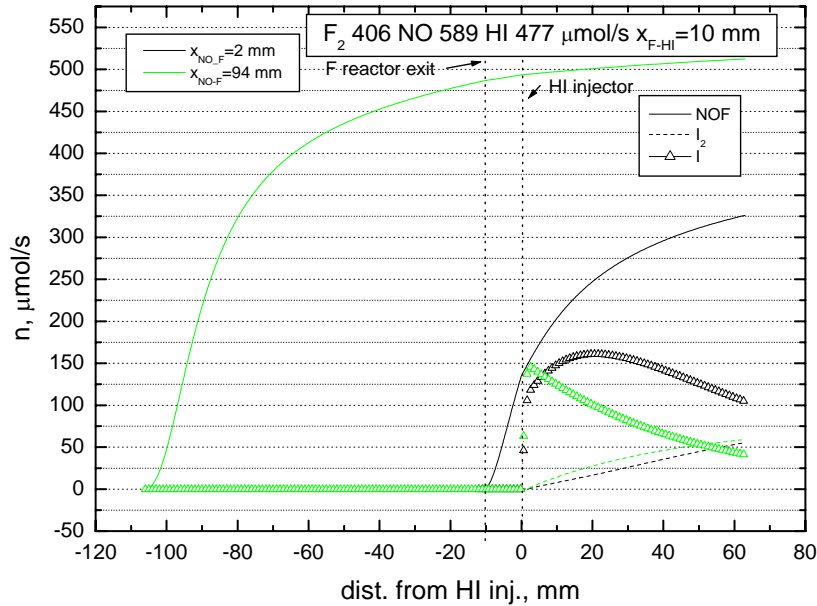
With respect to the recent experimental results with 20% F<sub>2</sub>/N<sub>2</sub> mixture and 100% NO and HI, a new modeling was performed with a variable distance between NO injection and the exit of coaxial F reactor ( $x_{NO-F}$ ). The calculated rates of atomic iodine production for three values of  $x_{NO-F}$ , corresponding to the time interval  $\tau_{NO-F} = 0.01, 0.16$  and  $0.47$  ms, respectively, are shown in **Fig. 17**. Experimental results on I concentration for these time intervals are presented in Fig. 13.



**Fig. 17.** Calculated production rate of F and I atoms at different distances between NO injector and exit of F reactor

It can be seen that the effect of  $\tau_{NO-F}$  on calculated maximum production rate is rather weak. This can be explained as follows: at short time interval,  $\tau_{NO-F}$ , the reaction (F-1) takes place predominantly in the outer (atomic I) reactor, where it runs slower than in the inner (F-) reactor. On the other hand, F atoms are instantly depleted there by the reaction with HI, and their loss in the reactions F-3 and 4 is low. At longer time intervals,  $\tau_{NO-F}$ , there is a faster production of F atoms in the inner reactor (at a higher pressure), leading to a faster production of reaction heat, which favors production reaction (F-1) against (F-2 and 3).

A higher pressure in the reactor has also the opposite effect because the concentration of F atoms reaches its maximum yet in the inner reactor. The concentration profile of atomic and molecular iodine, as well as NOF, at different  $x_{NO-F}$  is shown in **Fig. 18**.

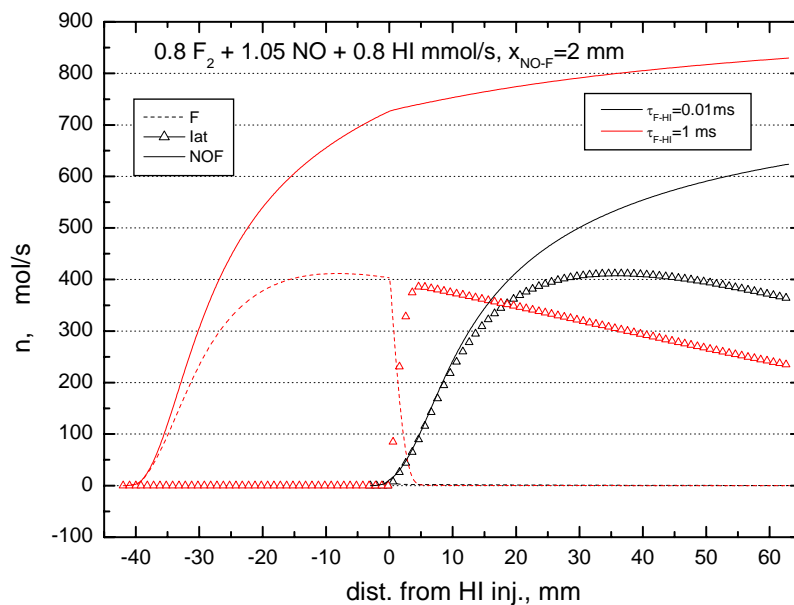


**Fig. 18.** Calculated production rate of I, NOF and  $I_2$  at two different distances between NO injector and exit of F reactor

At  $x_{NO-F} = 2$  mm, the reactions proceed in the outer I reactor (at lower pressure), which results in lower production of NOF and higher integral amount of I atoms.

A time interval between the inner reactor exit and HI injector,  $\tau_{F-HI}$ , has a similar effect on I atoms production as the  $\tau_{NO-F}$  interval, except for the fact that the F atoms generation between F reactor exit and HI injection proceeds in a low-pressure volume. The dependence of the maximum I

production rate on this distance is thus somewhat weaker. The production rates for different distance,  $x_{F-HI}$ , corresponding to time intervals  $\tau_{F-HI}$  of 0.01 ms and 1 ms are shown in **Fig. 19**.



**Fig. 19.** Production rate of F and I atoms calculated for different distance between the exit of F reactor and HI injector

### 3. Modification of the COIL device for atomic I generation via F atoms

#### 3.1. General conditions

The modeling and experimental results showed that a subsequent admixing of reactants ( $F_2$ , NO, and HI) into the subsonic flow with  $O_2(^1\Delta_g)$  in COIL employed in the  $Cl \rightarrow I$  system, cannot be used for the  $F \rightarrow I$  system. A rather slow formation of F atoms followed by I atoms generation would be accompanied by fast I pumping and  $I^*$  quenching reactions in the  $O_2(^1\Delta_g)$ . This serious problem led us to considering other experimental arrangements:

1. To generate F atoms in a separate reactor (step 1) and inject F atoms into the primary  $O_2(^1\Delta_g)$  flow together with HI (step 2).
2. To generate I atoms in a separate reactor (step 1) and to inject atomic I into the primary  $O_2(^1\Delta_g)$  flow (step 2).

By our estimations, the first arrangement would have two significant limitations: (i) a very fast reaction of F atoms with water molecules coming from the  $O_2(^1\Delta_g)$  generator ( $k = 4.15 \times 10^{-11} \exp[-3300/RT]^4$ ), and (ii) the  $HI + O_2(^1\Delta_g)$  reaction that was proved during our investigation of the  $Cl \rightarrow I$  system (see Final Report<sup>1</sup>, chapter 1.3.2.).



The results present above have shown that a sufficiently high yield of iodine atoms can be attained with 20% F<sub>2</sub> and non-diluted NO and HI, and (F<sub>2</sub> + NO) + HI mixing order. It was also found that a loss of I atoms by heterogeneous recombination in the reactor walls and during injection into the primary flow is not great. **These conclusions from the experimental investigation were applied for designing a separate reactors fitting to our 5-cm-gain-length supersonic COIL.**

### 3.2. Parameters of the reactor for atomic I generation

A separate reactor for production of atomic iodine is designed to fit to the 5-cm-gain-length supersonic COIL in our laboratory and for the following input of primary gases: 40 mmol/s Cl<sub>2</sub> + 80 mmol/s He<sub>prim</sub>. The reactor should operate in the following experimental conditions:

- using 20% F<sub>2</sub>/N<sub>2</sub> mixture, and non-diluted NO and HI
- mixing (F<sub>2</sub> + NO + HI) in one reactor space or mixing (F<sub>2</sub> + NO) in one reactor space and HI admixing in the second reactor space
- a time interval between (F<sub>2</sub> + NO) mixing and the F reactor exit ,  $\tau_{\text{NO-F}} = 0.01$  (÷ 0.4) ms (at 20 kPa),
- a time interval between the F reactor exit and HI admixing  $\tau_{\text{F-HI}} = (0 \div) 1.1$  ms (at 4 kPa)
- a time interval between HI admixing and exit from I reactor  $\tau_{\text{HI-I}} = 0.4$  ms (at 4 kPa),

Total input into 2 reactors: 3.75 mmol/s F<sub>2</sub> + 15 mmol/s N<sub>2</sub> (in 20 % mixture),

4 mmol/s NO,

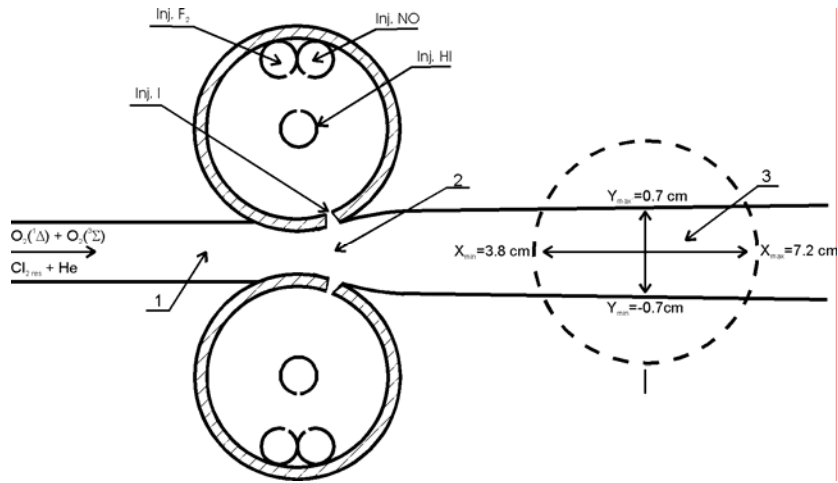
5 mmol/s HI or DI (DI is considered instead of HI because of much slower I<sup>\*</sup> quenching by DF),

- gas temperature in the reactor ~1100 K,
- expected exit from the reactor: 1.5 mmol/s atomic I

### 3.3. Reactor design

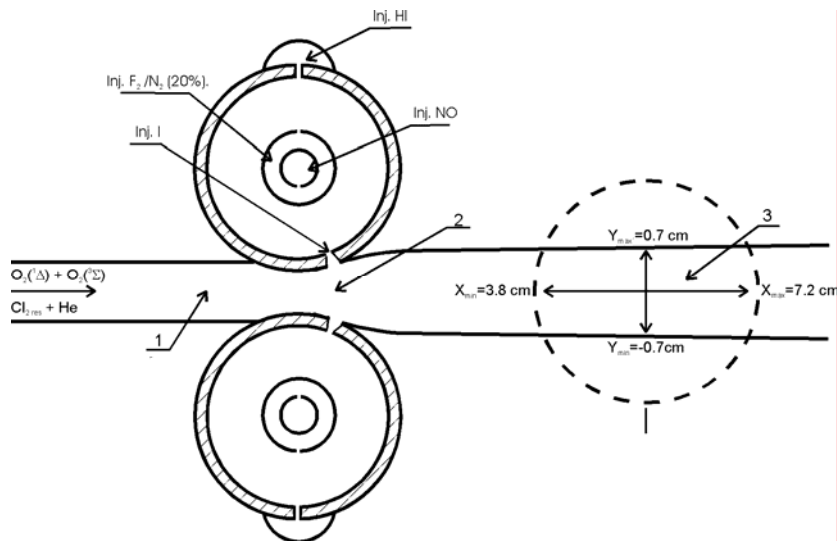
Two configurations of the reactor are proposed:

**A.** Two simple tubular reactors: all three gases are mixed together, and produced I atoms are injected into the primary O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) stream. The cross-section of this arrangement is shown in **Fig. 20**.



**Fig. 20.** The scheme of I atoms injection in a supersonic COIL (reactor A)

**B.** Two coaxial reactors consisting of inner reactors for F atoms production and outer reactors for  $F + HI$  (DI) reaction. The scheme of this configuration is shown in **Fig. 21**.



**Fig. 21.** The scheme of I atoms injection in a supersonic COIL (reactor B)

Technical drawings for the constructional design of these reactors fitting with our supersonic COIL are currently elaborated.

## 4. Conclusions from investigation of F→ I reaction system

### 10 % mixtures of reactants

- The maximum production of atomic iodine was obtained with the NO:F<sub>2</sub> ratio of 1:1 corresponding to stoichiometry of the reaction (F-1) generating F atoms.
- At the ratio NO:F<sub>2</sub> > 1, the rate of atomic iodine production was limited by F<sub>2</sub> flow rate. At NO:F<sub>2</sub> < 1 and HI:F<sub>2</sub> < 1, the concentration of atomic iodine dropped significantly with F<sub>2</sub> flow rate due to the reaction of I atoms with F<sub>2</sub> ( reaction F-13). This effect was weaker at higher HI flow rate, which was explained by additional generation of I atoms in the reaction of HI and F atoms formed in the reaction (F-13).
- At NO:F<sub>2</sub> < 1, the rate of atomic iodine production was limited by NO flow rate, while at NO:F<sub>2</sub> > 1, the generation of atomic F (and consequently atomic I ) was affected only slightly by NO flow rate due to a weak effect of loss-reactions (F-3 and 4).
- The rate of atomic I production grows with increasing HI flow rate at HI:F<sub>2</sub> < 1 and HI:NO < 1. This agrees with the kinetics of reaction (F-2) in the region of HI flow rate lower than the rate of F atoms production (“titration” of F atoms with HI). A significant excess of HI (vs. NO and F<sub>2</sub>) in the region of low pressure (1.5 – 2.5 kPa) did not reduce the production rate of I atoms (a low effect of loss-reaction (F-10)). At higher pressures (above about 8 kPa), the HI excess (together with N<sub>2</sub> in HI/N<sub>2</sub> mixture) reduced I production obviously due to the acceleration of ternary loss-reactions (F-3, 6, 8, 10 and 11).
- Atomic I production was significantly affected by the order of secondary gases (NO and HI) admixing into the primary F<sub>2</sub> flow. A higher rate of I production was obtained with the HI-NO injection order, which obviously caused a more uniform pre-mixing of HI before its reaction with F atoms (F-2), and suppressed the F atom loss in reactions with NO (F-3, 4).
- The time interval between F<sub>2</sub>+NO mixing and HI admixing may be prolonged up to 1 ms without a significant decrease in I production (at pressures up to 9 kPa (67 torr)), which proved a rather long lifetime of F atoms.
- Temperature of the reaction mixture was up to 700 K. It was influenced mainly by the F<sub>2</sub> flow rate due to exothermic reactions F<sub>2</sub>+NO and F<sub>2</sub>+I. An excessive NO and/or HI flows (mixed with N<sub>2</sub>) caused a slight decrease in the temperature due to a diluting effect of nitrogen.
- The highest rate of atomic iodine production was 180 μmol/s, and the yield of atomic I ranged from 6 to 30 % (related to F<sub>2</sub>) at HI-NO injection order. A maximum concentration of atomic iodine was 8 x 10<sup>15</sup> cm<sup>-3</sup> (at total pressure of 9 kPa (67 torr)) within a time interval

from 0.45 to 2 ms after admixing the last reactant. With the NO-HI injection order, a maximum I concentration was lower ( $5 \times 10^{15} \text{ cm}^{-3}$  at a pressure of 8 kPa (60 torr)).

### **20 % F<sub>2</sub>/N<sub>2</sub> mixture and non-diluted NO and HI**

- Using of less diluted reacting gases increased substantially the production of I atoms. The production rate was nearly directly proportional to a flow rate of the reactants up to a high total pressure (17 kPa (127 torr)).
- The production rate was not significantly affected by the time delay between F<sub>2</sub> + NO mixing in the F reactor up to 1.1 ms (at 8.5 kPa). Also the time interval up to 1.1 ms between F atoms injection into I reactor and HI admixing had no negative effect (at 4.2 kPa in the I reactor). Both results agree with results of modeling, and proved a rather long lifetime of F atoms.
- High concentrations of atomic iodine were obtained (up to  $1.6 \times 10^{16} \text{ cm}^{-3}$ ) in these conditions, and the I yield was 47 % (related to F<sub>2</sub>) or 34 % (related to HI).
- Experiments with F<sub>2</sub> + HI reaction system resulted in an estimate of its rate constant of  $1.5 \times 10^{-14} \text{ cm}^{-3}$  at 670 K.
- The rate of wall recombination of I atoms was estimated from their loss on a fine stainless steel mesh, through which the gas passed. These results supplied by modeling of the reaction system has shown that the wall recombination of both F atoms and I atoms is controlled by diffusion. Owing to this mechanism their loss through the wall recombination in the reactor and during gas injection is less than 10 %.
- Parameters of the separate reactor for atomic iodine generation for the 5cm-gain-length COIL were estimated.
- A design of two types of reactors for atomic iodine generation in the supersonic 5 cm-gain-length COIL was proposed.

## **II. Gain measurements in COIL with atomic iodine generated via Cl atoms**

### **1. Experimental**

The supersonic COIL device was modified for chemical generation of atomic iodine in the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) flow from the singlet oxygen generator. Injectors of gaseous reactants were located in the rectangular subsonic channel. The injector of ClO<sub>2</sub> formed by a horizontal tube of 8 mm in diameter and with two rows of 0.7 mm-holes was placed in the channel center close the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) generator

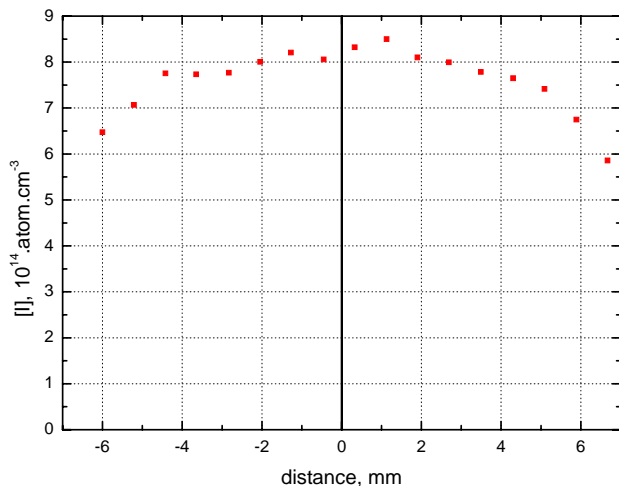
exit and 18 cm upstream of the slit nozzle throat. Injectors of NO and HI in the form of rectangular tubes were installed in the channel bottom and ceiling close to the nozzle throat. One row of 0.7 mm holes and one row of 0.5 mm holes was drilled in both injectors, and the rows with 0.5 mm holes were 0.9 cm and 0.35 cm, respectively, distant from the throat. The injectors need not to be heated. The gaseous mixture containing reaction products including generated atomic iodine and  $O_2(^1\Delta_g)$  in the flow was choked and expanded to Mach number about 2 in the slit nozzle with the cross-section of 5 x 0.67 cm. The axis of optical resonator was 5.5 cm downstream of the nozzle throat.

The concentration of atomic iodine and gain were measured in the gain region of optical resonator by means of the Iodine Scan Diagnostics (ISD). The ISD probe beam was directed horizontally and perpendicularly to the gas flow. The gain could be mapped either stream wise in the region within 38 – 72 mm from the nozzle throat, or perpendicularly to the gas flow direction between the cavity bottom and ceiling. Two wedged shaped windows ( $3^\circ$ ) were fixed in the resonator arms each of inner length of 10.6 cm.

The gaseous  $ClO_2$  was diluted 1:10 with  $N_2$  (chlorine for  $ClO_2$  production by its reaction with  $NaClO_2$  was diluted 1:16). The  $NO/N_2$  mixture and about 5 %  $HI/N_2$  mixture were delivered from gas cylinders. Flow rates of gases were measured by calibrated flow meters with diaphragm orifice. Gas exiting the laser passed through a liquid nitrogen trap and was exhausted with a Roots pump of the capacity  $0.83 \text{ m}^3 \text{ s}^{-1}$ .

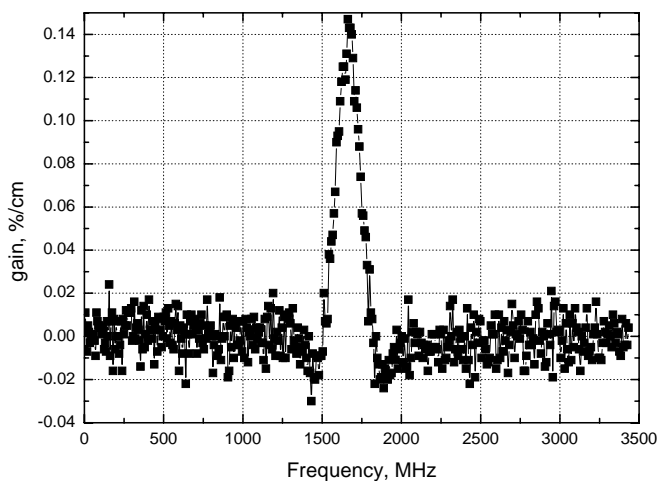
## 2. Experimental results

In the first set of experiments, the gain was measured at conditions typically employed during lasing. An example of the profile of atomic iodine concentration across the cavity is in **Fig. 22** that was obtained at pressure of 350 Pa (2.6 torr) and gas temperature 210 K. Windows of the cavity were not purged in these experiments. Fig. 22 shows that atomic I concentration was rather high. The small signal gain measured at about the same flow rates of these gases and 40 mmol/s of chlorine input into the  $O_2(^1\Delta_g)$  generator was however rather low. The maximum gain value was  $0.23 \text{ \% cm}^{-1}$ , and in the cavity center there was a minimum on its profile. Also the gas temperature evaluated from these measurements was non-realistically low – between 80 and 180 K.



**Fig. 22.** Concentration of atomic iodine across the cavity (0 distance is the cavity center); gas flow rate (in  $\text{mmol s}^{-1}$ ): 1.5  $\text{ClO}_2$ , 4  $\text{NO}$ , 2  $\text{HI}$ , 69  $\text{N}_{2(\text{sec})}$ , and 130  $\text{He}_{\text{prim}}$

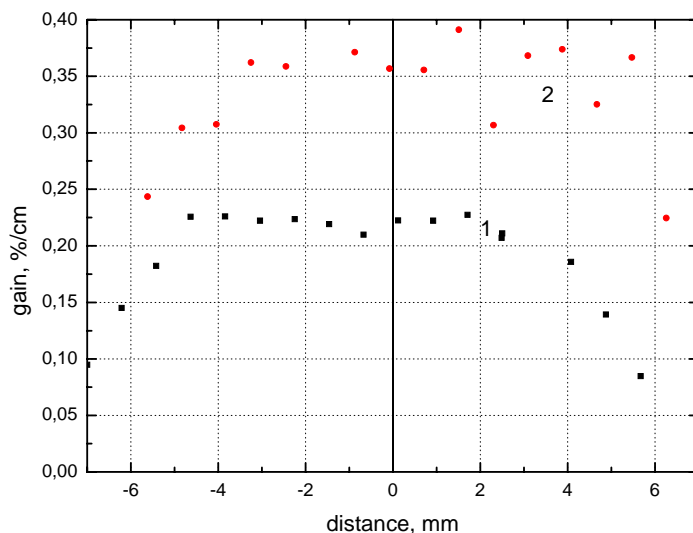
The gain-frequency curves recorded by ISD showed a deformed shape as can be seen in **Fig. 23**.



**Fig. 23.** Gain – frequency curve recorded in ISD measurements; gas flow rate (in  $\text{mmol cm}^{-1}$ ): 1.5  $\text{ClO}_2$ , 4.2  $\text{NO}$ , 1.9  $\text{HI}$ , and 40  $\text{Cl}_2$ , 100  $\text{He}_{\text{prim}}$

The shape of the gain curve with a central maximum and two minima resulted probably from a superposition of the narrower emission and broader absorption curve. This can be explained by the presence of I atoms in the ground state except I atoms in the excited state. The probe beam could pass through an inhomogeneous medium - a region(s) containing mostly  $\text{I}^*$  atoms (with a lower temperature), and region(s) containing mostly I atoms (with a higher temperature). It was revealed

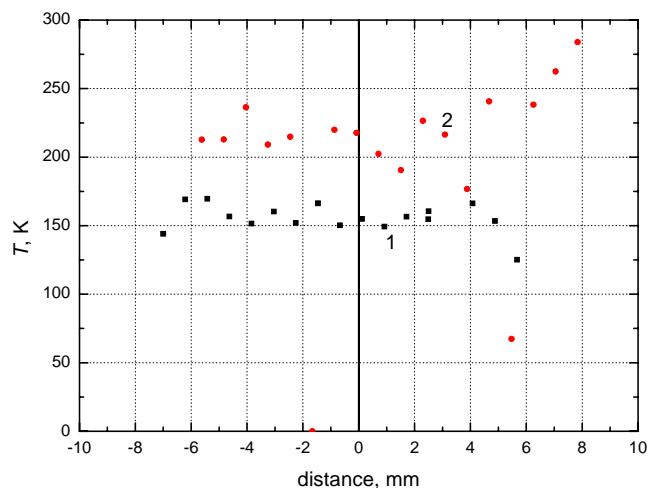
that this phenomenon could be obviously caused by ground state iodine atoms present in the resonator arms that were an inner length of 10.7 cm. The next gain measurements were therefore performed with purging of the optical windows to protect a penetration of iodine from the main flow into the arms. **Fig. 24** shows the gain profiles across the cavity recorded either with the purging by N<sub>2</sub> (5 mmol/s) or without it.



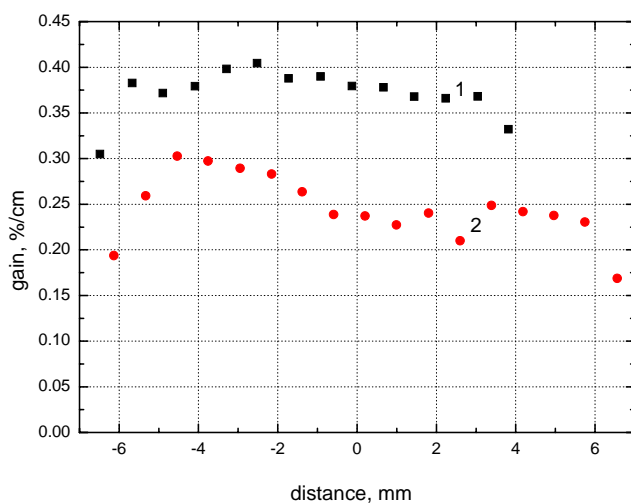
**Fig. 24.** Gain profile measured without windows purging (curve 1) and with purging (curve 2); gas flow rate (in mmol cm<sup>-1</sup>): 1.5 ClO<sub>2</sub>, 4 NO, 1.3 HI, 20 Cl<sub>2</sub>, and 87 He<sub>prim</sub>

Also the gas temperature evaluated from measurements with purging had the anticipated realistic values (**Fig. 25**). The results in Figs. 24 and 25 document that a purging of the resonator arms is very favorable for increasing the gain.

The effect of chlorine flow rate in the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) generator on the gain can be seen in **Fig. 26**. The temperature evaluated from both measurements was approximately the same (~ 210 K).



**Fig. 25.** Gas temperatures measured without windows purging (curve 1) and with it (curve 2), conditions as in Fig. 24



**Fig. 26.** Gain profile measured at  $20 \text{ mmol cm}^{-1} \text{ Cl}_2$  (curve 1) and  $32 \text{ mmol cm}^{-1} \text{ Cl}_2$  (curve 2); gas flow rate (in  $\text{mmol cm}^{-1}$ ): 1.4  $\text{ClO}_2$ , 4.1  $\text{NO}$ , 0.9  $\text{HI}$ , and  $89 \text{ He}_{\text{prim}}$

The lower gain at higher  $\text{Cl}_2$  flow rate reflects a lower  $\text{O}_2(^1\Delta_g)$  yield, which was proved by the  $\text{O}_2(^1\Delta_g)$  yield measurement for 3 different  $\text{Cl}_2$  flow rates (Table 1).

**Tab. 1**  
Yield of  $\text{O}_2(^1\Delta_g)$  vs.  $\text{Cl}_2$  flow rate  
 $86 \text{ mmol/s He}$ ,  $P_{\text{gen}} = 9 \text{ kPa}$  (67.5 torr)

$n_{\text{Cl}_2}$ , mmol/s	25	32	47
$Y_{\Delta}$ , %	78	70	60



The small signal gain can be calculated by the equation<sup>5</sup>

$$\alpha_{3-4} = \sigma_{3-4} [(2K_{eq}+1)\eta_{\Delta} - 1] / \{2 [(K_{eq}-1)\eta_{\Delta} + 1]\} c_I,$$

where the cross section for the 3-4 transition equals to

$$\sigma_{3-4} = 1.3 \times 10^{-16} / T^{1/2}$$

and the equilibrium constant

$$K_{eq} = 0.75 \exp(401.4/T)$$

The small signal gain calculated for the measured mean concentration of I atoms  $c_I = 7.5 \times 10^{14} \text{ cm}^{-3}$ , temperature 210 K, and various  $O_2(^1\Delta_g)$  yield is given in Table 2.

**Tab. 2**  
Small signal gain calculated for different  $O_2(^1\Delta_g)$  yield

$Y_{\Delta}, \%$	0.4	0.5	0.6	0.7	0.78
$g_{3,4}, \% \text{ cm}^{-1}$	0.44	0.51	0.56	0.6	0.62

It is obvious from Tables 1, 2 and Fig. 25 that the calculated gain decreases with decreasing  $O_2(^1\Delta_g)$  yield, and with increasing chlorine flow rate, respectively, which is in accordance with the experimental results. It should be noted that the calculated values of the gain are rather higher than the data measured with chemically generated atomic iodine. This can be explained by the reaction



in which produced  $HO_2$  radical can quench singlet oxygen. By this undesirable process, the  $O_2(^1\Delta_g)$  concentration in the laser cavity can be reduced, and the gain as well. This process was discussed in more detail in Final Report<sup>1</sup> (chapter 1.3.2.). Avoiding or suppressing the effect of the reaction (Cl-1) led us to a decision to generate atomic iodine for the COIL operation in a separate reactor and inject it into the primary flow with  $O_2(^1\Delta_g)$ . This reactor was already designed and fabricated, and is prepared currently for using in further experimental investigation.

### 3. Conclusions from investigation of Cl → I reaction system

- Employing the purging of resonator windows had a substantially positive effect on the shape of measured gain-frequency curves and also on the gain values.
- The difference between calculated and measured gain was explained by a negative effect of reaction (Cl-1) between HI and  $O_2(^1\Delta_g)$ .

- To suppress the effect of this reaction, a new reactor for I atoms production separated from the  $O_2(^1\Delta_g)$  flow was designed and fabricated fitting with our COIL device.

## References

1. Final Report of the grant SPC # 02-4040, submitted 16 Jan 2004
2. Interim Report 001 of this grant, submitted 23 Feb 2004
3. Interim Report 002 of this grant, submitted 23 June 2004
4. C.D.Walther, H.G. Wagner “Über der Reaktionen von F-atomen mit  $H_2O$ ,  $H_2O_2$ , und  $NH_3$ “ Ber. Bunsenges. Phys. Chem. **87**, 106 (1983)
5. G.D. Hager, C.A. Helms, K.A. Truesdell, D. Plummer, J. Erkkila, P. Crowell, “A simplified analytical model for gain saturation and power extraction in the flowing chemical oxygen-iodine laser”, IEEE J. Quant. Electr. **32**, 1525 (1996)

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We thank very much Dr. Gordon Hager, the grant supervisor, and Dr. Timothy Madden, Research Scientist at the US AFRL/DE for their encouragement in our work, and beneficial discussions on the grant tasks.

## Cost Proposal


<b>1. Expendable supplies and materials:</b>			\$9,000
Gases and chemicals (HI gas, NO/N <sub>2</sub> , F <sub>2</sub> /N <sub>2</sub> , Helium, H <sub>2</sub> O <sub>2</sub> , KOH), vacuum accessory and special oil for Aggressive gases (F <sub>2</sub> , Cl <sub>2</sub> , HI), constructional materials			
Office, computers and printers supplies		\$4,000	
(Controlling cards National Instruments for ISD diagnostics)			
<b>2. Travel:</b>			
Within Europe			\$1,100
<b>3. Publications in Journal, Reports, and Literature purchased:</b>			\$500
Preparation of papers and reports		\$200	
Literature purchasing		\$300	
<b>4. Labor-rewards:</b>			\$11,000
Jarmila Kodymová (PI)	600 hrs @ \$5,0/hr	\$3,000	
Otomar Špalek (PI)	600 hrs @ \$5,0/hr	\$3,000	
Vít Jirásek	600 hrs @ \$3,8/hr	\$2,300	
Miroslav Čenský	600 hrs @ \$3,8/hr	\$2,100	
Technicians	200 hrs @ \$2,5/hr	\$500	
<b>5. Overheads charges to the Institute</b>			\$2,400
<b>Total cost proposal</b>			<b>\$24,000</b>


Dr. Jarmila Kodymová  
Principal Investigator

Ing. Karel Jungwirth, DrSc.  
Director of Institute of Physics

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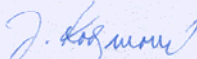
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## DECLARATION

- (1) **The Contractor, Institute of Physics of the Academy of Sciences of the Czech Republic, hereby declares that, to the best of its knowledge and believes, the technical data delivered herewith under Contract No. FA8655-03-1-3A63 is complete, accurate, and complies with all requirements of the contract.**
  
- (2) **I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this Contract.**


Date: 23 October 2004

Name and Title of Principal Investigator:

  
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Name and Title of Authorized Official:

  
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Director of Institute of Physics AS