Application of ARAS on the oxygen atoms in chemical kinetics of high temperature reactions

A. Emelianov[1], N. Bystrov[1], A. Eremin[1], P. Yatsenko[1,2]

[1]Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia
[2]Bauman Moscow State Technical University, Moscow, Russia
aemelia@ihed.ras.ru

Motivation

The formation of atomic oxygen occurs in most hydrocarbon and biofuel combustion processes. Various kinetic schemes make it possible to quantitatively calculate the appearance and consumption of atomic oxygen during proceeding reactions. However, the verification of these models is based on accurate experimental data obtained under various conditions. One of the most reliable instrument for experimental study in chemical kinetics is the shock tube. The method of atomic resonance absorption spectroscopy (ARAS), is the gold standard of chemical kinetics and makes it possible to directly and reliably measure the concentration of atomic oxygen with the possible range of the measured concentration within $3 \cdot 10^{11}$-10^{14} cm^3. As a result the rate constants of the reactions of various oxygen-containing compounds can be directly determined.

Goal of work

Development of application of O-ARAS diagnostics in the shock tubes, in the wide range of reactions from dissociation of simple molecules to pyrolysis and combustion reactions of alcohols complex compounds at temperatures of 1200-2500 K and pressures of 2-4. bar.

Decomposition of small molecules

Reaction	Log$_{10}$A (cm^3/s·mol)	n	E/R K	Temp.range	Ref
CO = C+O	19.96	-3.1	129000	5500--9000	Duisburg
CO$_2$ = CO+O	13.40	-	43800	2500--3400	Nagaoka
	14.56		52500	2400--4400	Duisburg
N$_2$O = N$_2$+O	14.97	-	29900	1700--2500	Stuttgart
	15.16	-	30800	1850--2500	Duisburg
	14.70	-	29000	1300--2500	Dayton
	15.0	-	30400	1600--2500	Nagaoka
	14.50	-	27900	1540--2500	Argonne
	14.85	-	29100	1200--2380	New York
	14.86	-	28878	1490--2490	Orleans
	14.7	-	28500	1760--2500	Moscow
O$_2$ = O+O	12.50	-	48200	2850--5550	New York
	15.73	1.0	59400	2370-4160	Duisburg
	14.53	-	55700	2740-4530	Orleans
SO$_2$ = SO+O	15.47	-	50450	2188--4249	Taiwan
	16.45	-	58600	2500--3400	Stuttgard

Absorption cross section of N$_2$0 at different temperature at 130.5 nm

Duisburg (Roth P. Kruse T., Burmeister M., Gulati S.K., Natarajan K., Thielen K., Mozzhukin E., Mick H., Giesen A., Takahashi K., Herzler J., Jerig L.)

Tokyo (Matsui H., Koshi M., Ohmori K., Yoshimura M., Kamiya K., Tsuchiya K., Asaba T., Shina H., Miyoshi A., Kamiya K., Lee P.F., Chen W.Y., Wang N.S.,)

Reactions studied with O-ARAS

Reaction	Temp. range	Ref
C + NO = CN + O	1550--4050	Stanford
C + O$_2$ = CO + O	1500--4200	Stanford
C$_2$ + NO = products	3150--3950	Duisburg
CH$_2$ + O$_2$ = CH$_2$O + O	1850--2050	Tokyo
CN + O$_2$ = CNO + O	2700--3800	Stanford
	2160--2750	Duisburg
CO + O$_2$ = CO$_2$ + O	1700--3500	Duisburg
	1000--1400	Hashirimizu
	1200--2200	Moscow
CH$_3$ + O$_2$ = CH$_3$O + O	1400--2300	Göttingen
	1430--2150	Hiroshima
	1622--1840	Tokyo
	1600--2100	Argonne
CH + NO = CHN + O	2570--3790	Stanford
H$_2$S + O$_2$ = products	1400--1850	Tokyo
N$_2$ + O$_2$ = N$_2$ + O + O	2740--3460	Orleans
NH$_2$ + O$_2$ = NH$_2$O + O	1450--2300	Göttingen
NO + N = N$_2$ + O	1251--3152	Argonne
	1750--1360	Duisburg
NO + NO = N$_2$O + O	2600--6300	New York
	2700--3500	Tokyo
	2400--6200	Duisburg
H + O$_2$ = OH + O	1700--2500	Stuttgard
OH + O$_2$ = HO$_2$ + O	1950--2100	Argonne
OH + OH = H$_2$O + O	1288--2033	Brookhaven
S + O$_2$ = SO + O	1900--2200	Hiroshima
	1220--3460	Duisburg
	980--1610	Tokyo
Sn + O$_2$ = SnO + O	1300--2250	Duisburg
SnO + O$_2$ = SnO$_2$ + O	1700--2300	Duisburg
SO + O$_2$ = SO$_2$ + O	2570--2980	Duisburg
CH$_4$ + N$_2$O = products	1890--3250	Moscow
n-C$_4$H$_9$OH + N$_2$O = products	1890--3250	Moscow
CH$_3$OCH$_3$ + N$_2$O = products	1890--3250	Moscow
n-C3H7OH + N$_2$O = products	1700--3200	Moscow
i-C3H7OH + N$_2$O = products	1700--3200	Moscow
C$_2$H$_2$ + N$_2$O = products	1800--3200	Moscow

The possibilities of using high-power excimer lasers at a wavelength of 193 nm for photolysis of simple oxygen compounds

$$f = \sigma \frac{E}{h\nu} \frac{T}{273}$$ - the fraction of absorbing molecules

$\frac{E}{h\nu}$ - number of excimer photons per unit area [cm^{-2}], $E = 500$ mJ $\sim 5 \cdot 10^{17}$ photons

$$g = \sigma N_L P X_0 L$$ - the initial optical depth

σ - absorption cross section, N_L - 2.69×10^{19} [atm^{-1} cm^{-3}] Loschmidt's number, P - pressure [atm], X_0 - mole fraction of the absorbing species prior to photolysis, L - length of the photolysis volume along the axis of the shock tube.

If g is small, then the product profile will be uniform

Calculated inhomogeneity of the product mole fraction profile depending on the initial optical thickness g

New York (Watt W.S., Myerson A.L., Ross S.K., Sutherland J.W., Kuo S.C., Klemm R.B.)

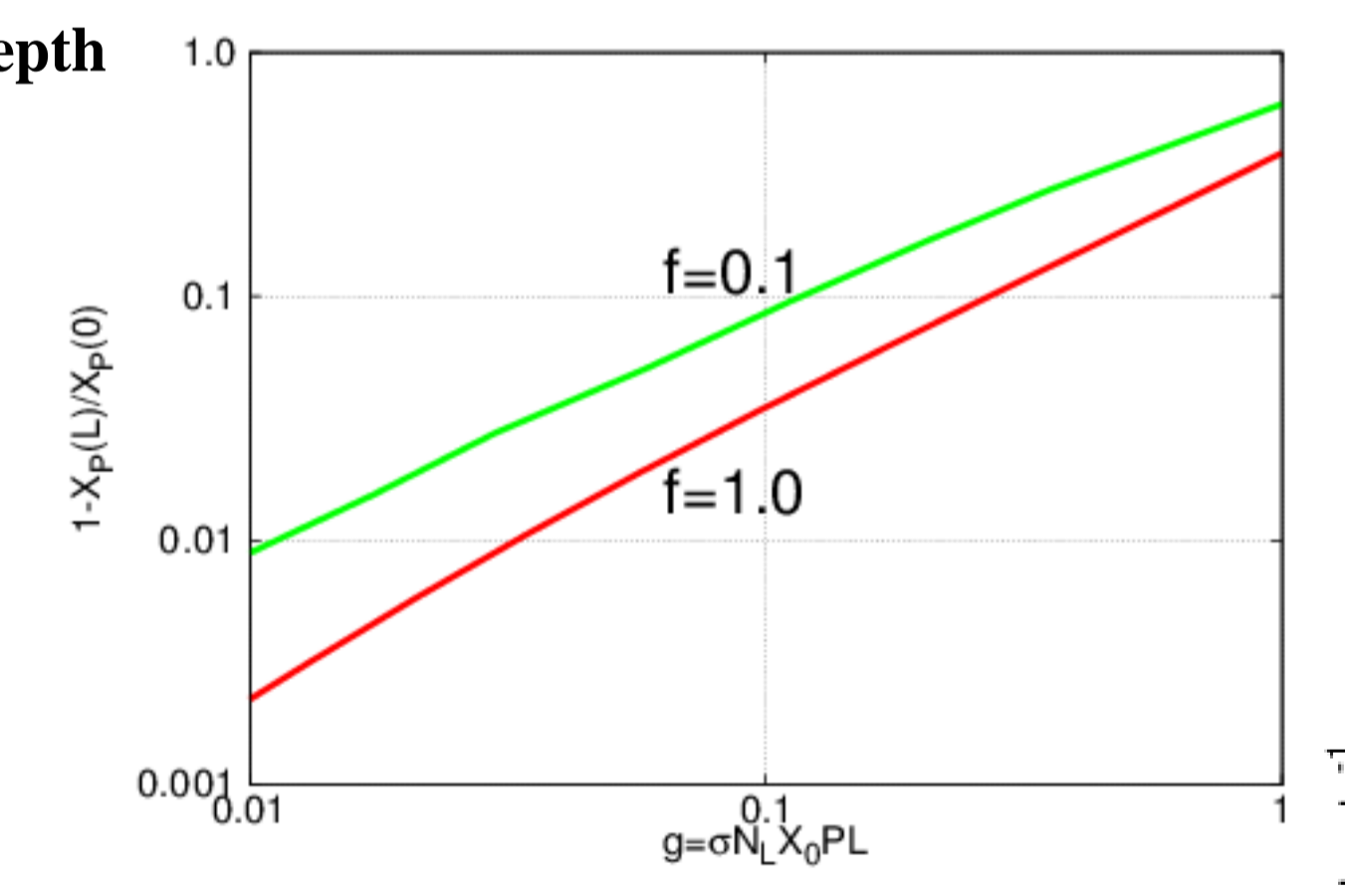Argonne (Michael J.V., Kumaran S.S., Su M.C., Lim K.P., Srinivasan N,K., Sutherland J.W.)

Göttingen (Wagner H.Gg., Klatt M., Röhrig M., Henning G., Spindler B.)

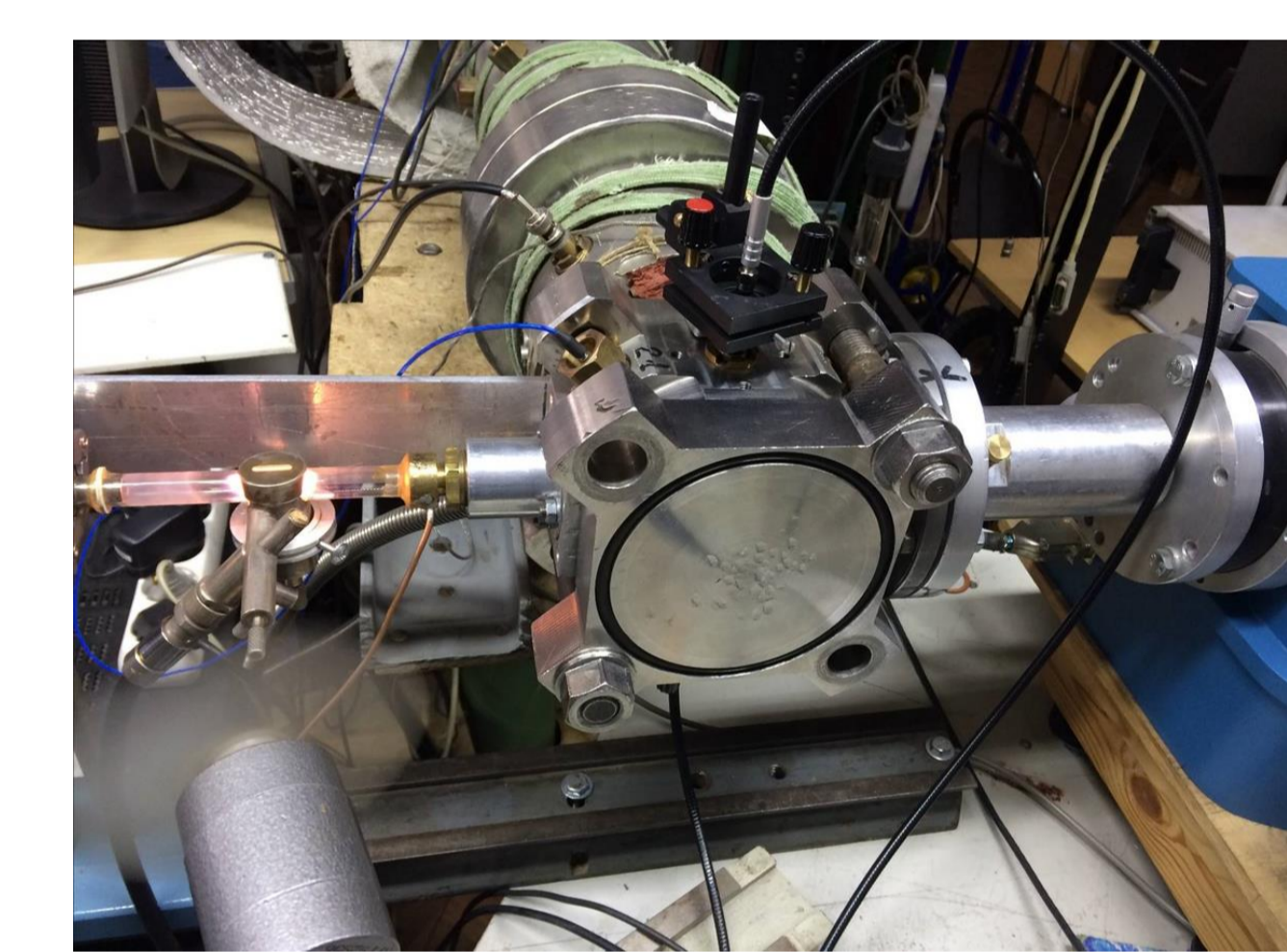Hiroshima (Saito K., Ito R., Kakumoro T., Imamura A., Ueda Y.)

Brookhaven (Sutherland J.W., Patterson P.M., Klemm R.B.)

Orleans (Paillard C.E., Abid S., Naudet V., Javoy S.)
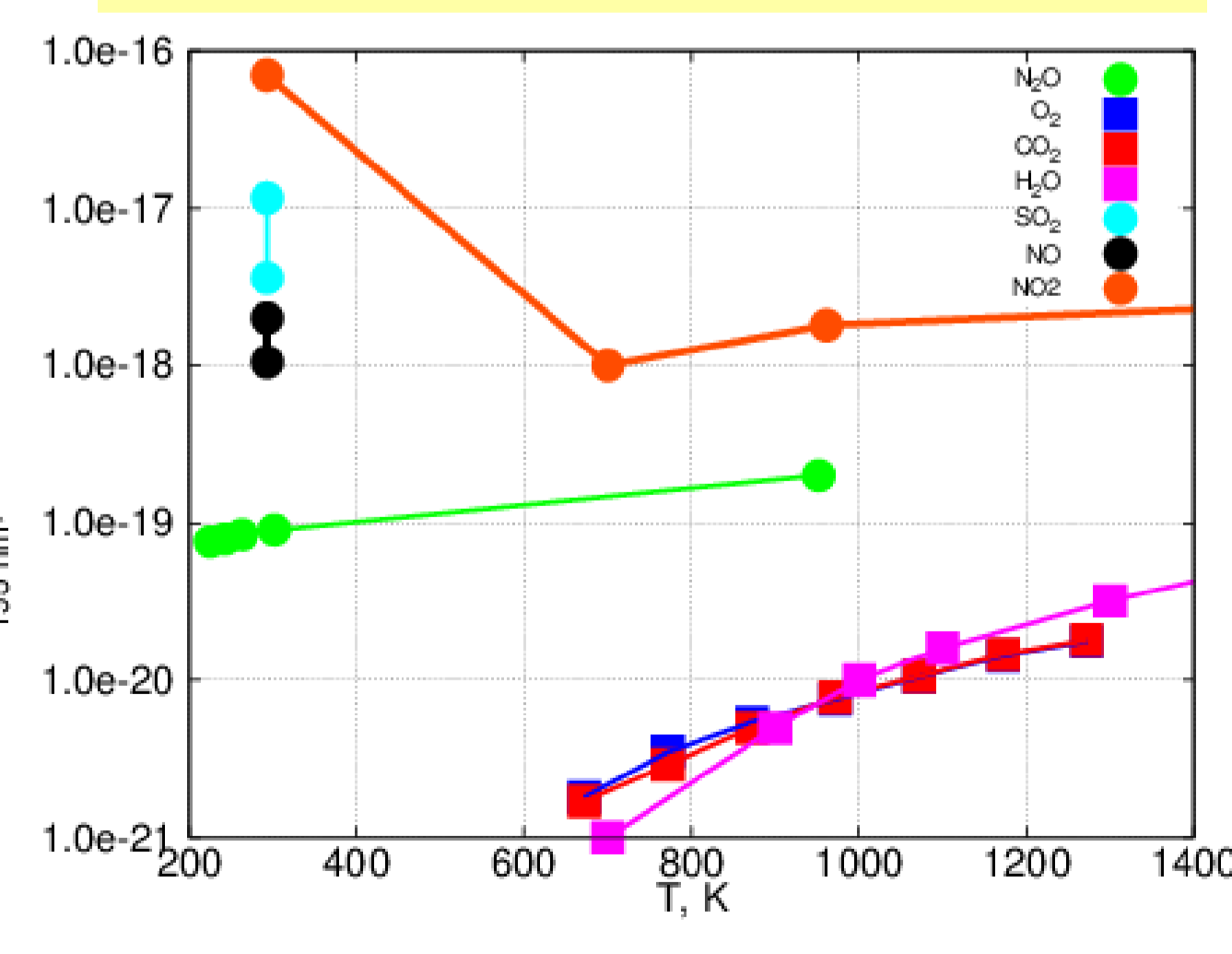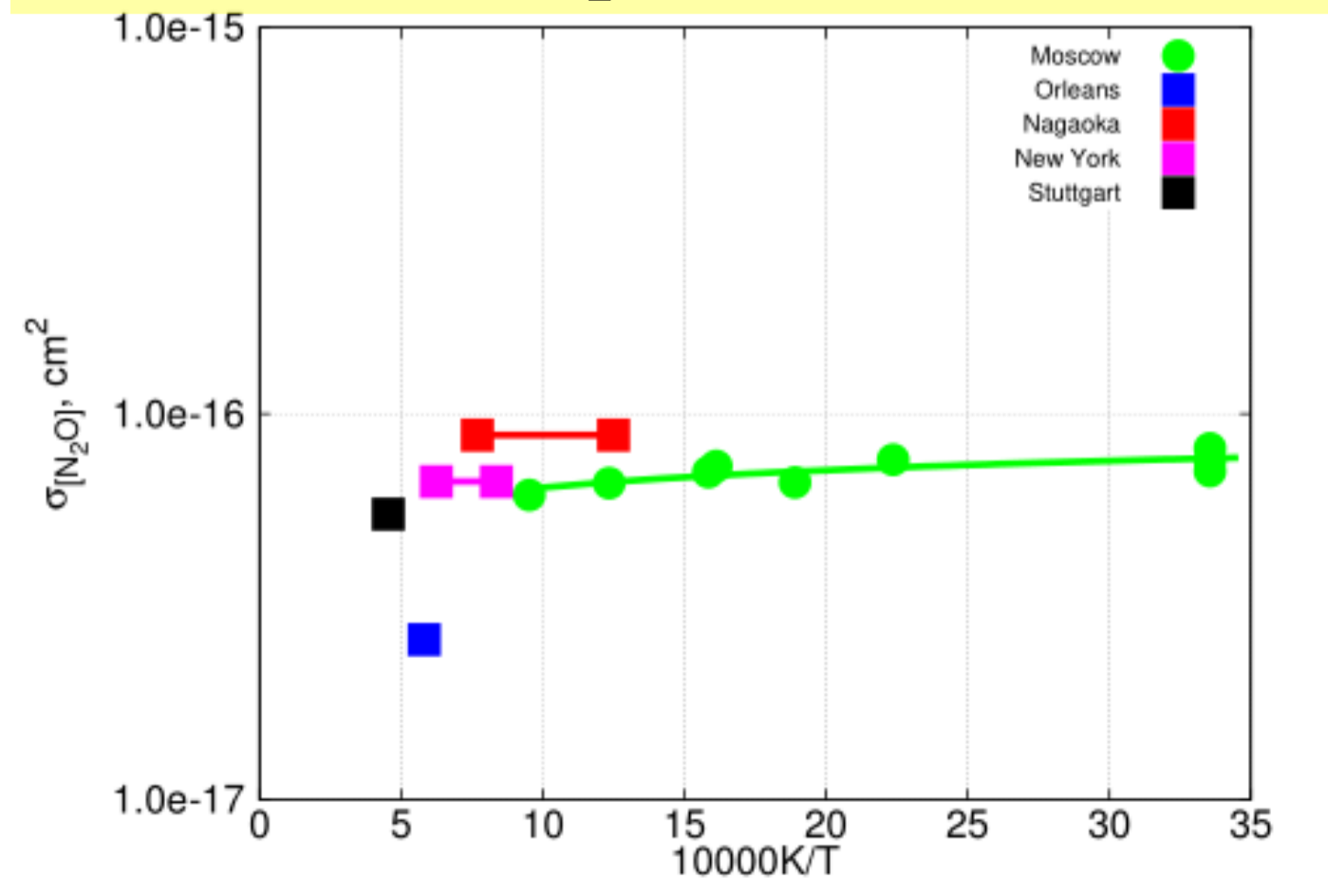
Hagaoka (Fujii N., Sagawai S., Sato T., Nosaka Y., Miyama H.)

Dayton (Lifshitz A., Skinner G.B., Wood D.R., Pamidimukkala K.M.)

Stanford (Hanson R.K., Dean A.J., Bowman C.T., Davidson D.F., DiRosa M.D.)

Taiwan (Lu C.W., Wu Y.J, Lee Y.P., Zhu R.S., Lin M.C.)

Stuttgard (Just Th., Frank P., Rimpel G.)

Hashirimizu (Koike T.)

Experiment setup

Absorption cross section of oxygen compounds at different temperature on 193 nm