Experimental and numerical study of the structure of $NH_3/H_2/O_2/Ar$ flames at elevated pressures

Ksenia N. Osipova, Andrey G. Shmakov

Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk

Novosibirsk State University, Novosibirsk

N* Novosibirsk
State
University
*THE REAL SCIENCE

2022

X International Voevodsky Conference "Physics and Chemistry of Elementary Chemical Processes" (VVV-2022)
05-09 September, 2022, Novosibirsk, Russia

Introduction

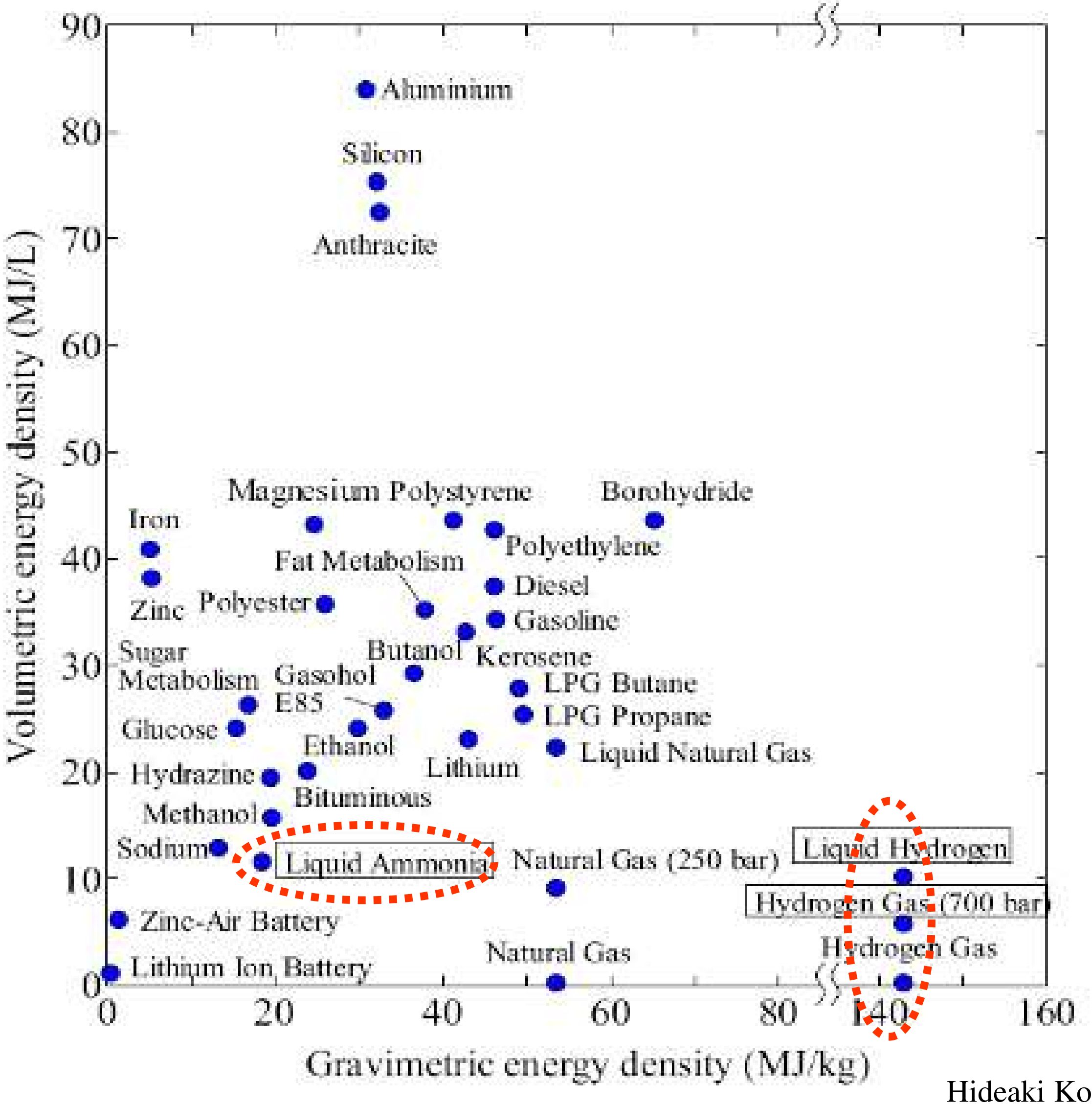
Modern view on alternative fuels - ecological aspect

Alternative fuels

- **Liquid biofuels(alcohols, biodiesel)**
- **Dimethyl ether**
- ***Hydrogen****

Introduction

Gravimetric and volumetric energy density of flammable materials and batteries



Hideaki Kobayashi, PCI, 2018

Introduction

Problems associated with hydrogen implementation for transportation

Cryogenic tank for liquid hydrogen

T=−252.8 °C

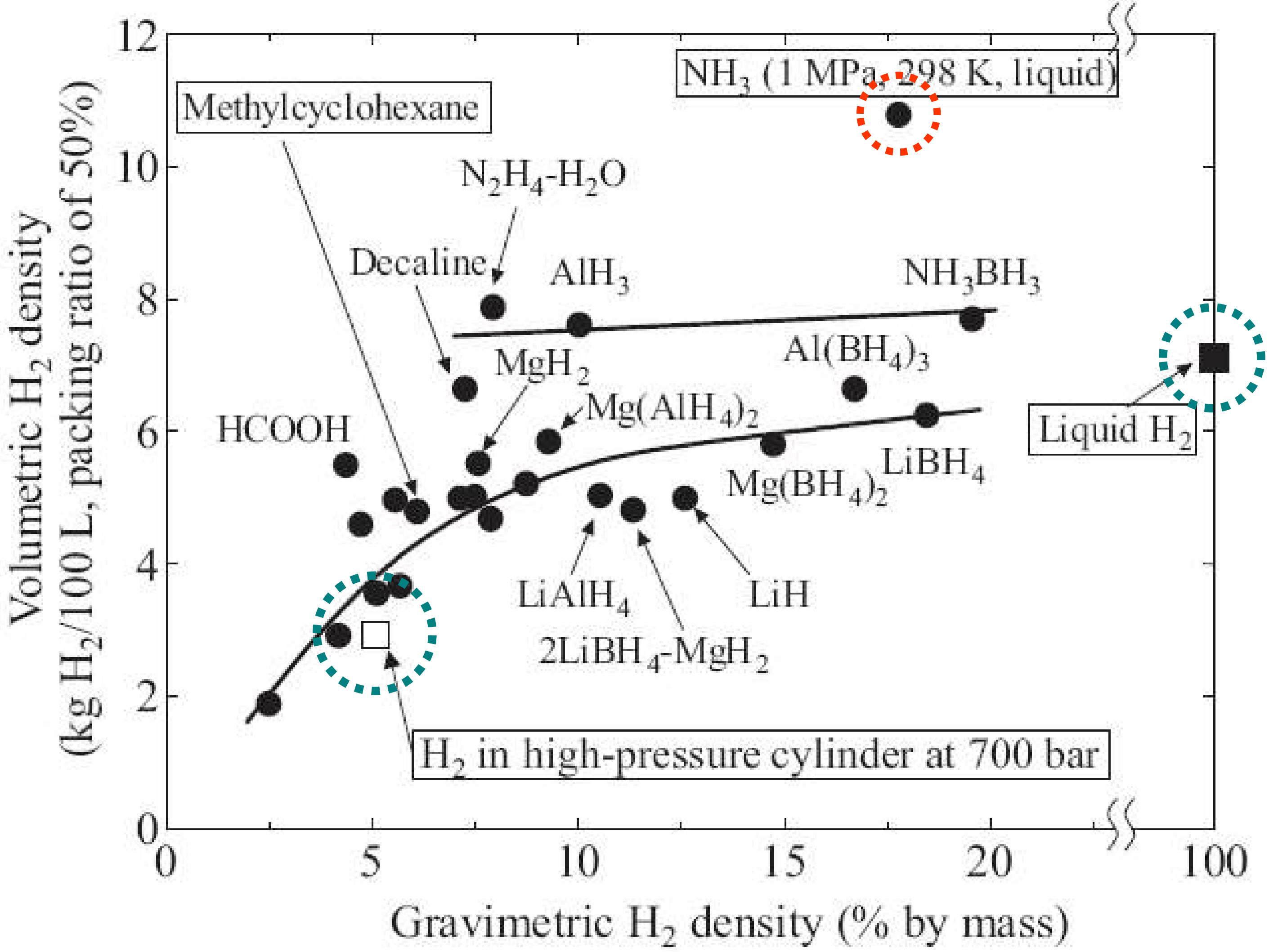
V=50 l.,

P=150 atm,
m_6=77 kg,
m_{H2}=0.67 kg
(0.87% от m_6)

- **leakage through small holes, no odor**
- **burning velocity of H_2/air flames-up to 3 m/s**
- **flammability limits – from 4 to 75%**

Introduction

Gravimetric and volumetric density of hydrogen carriers



Hideaki Kobayashi, PCI, 2018

Introduction

Liquid **ammonia**:-33 °C, 1 atm or 8-10 atm , T_{room}.

Ammonia/air flames: low burning velocity

(≈7cm/s at 298K and 1 atm), high ignition energy

↓

The addition of small amount of hydrogen to ammonia

- ***Reliable experimental data on combustion and oxidation of ammonia/hydrogen blends are extremely important, especially at high pressures***

Introduction (NH_3/H_2 blends)

1) B. Shu et al. Proc. Combust. Inst., 2019.
2) O. Mathieu et al. Combust. Flame., 2015.
3) L. Dai et al. Combust. Flame., 2020.

Ignition delay time

1) J.H. Lee. Int. J. Hydrog. Energy., 2010.
2) A. Ichikawa, Int. J. Hydrog. Energy., 2015.
3) J-B. Lee, Int. J. Hydrog. Energy., 2010.
4) S. Wang et al. Combust. Flame., 2020.
5) C. Lhuillier et al. Fuel., 2020.
6) B. Mei et al. Combust. Flame., 2021.
7) K.P. Shrestha et al.,Proc. Combust. Inst., 2021
8) G.J. Gotama et al., Combust. Flame 2022

Laminar flame speed

1) X. Zhang et al. Combust Flame, 2021.
2) K.N. Osipova. Fuel., 2021.

Oxidation in JSR

1) C. Duynslaegher . Proc. Combust. Inst., 2009.
2) C. Brackmann . Combust. Flame., 2016.
3) K.N. Osipova. Int. J. Hydrog. Energy., 2021.

Flame structure

The aims of the work

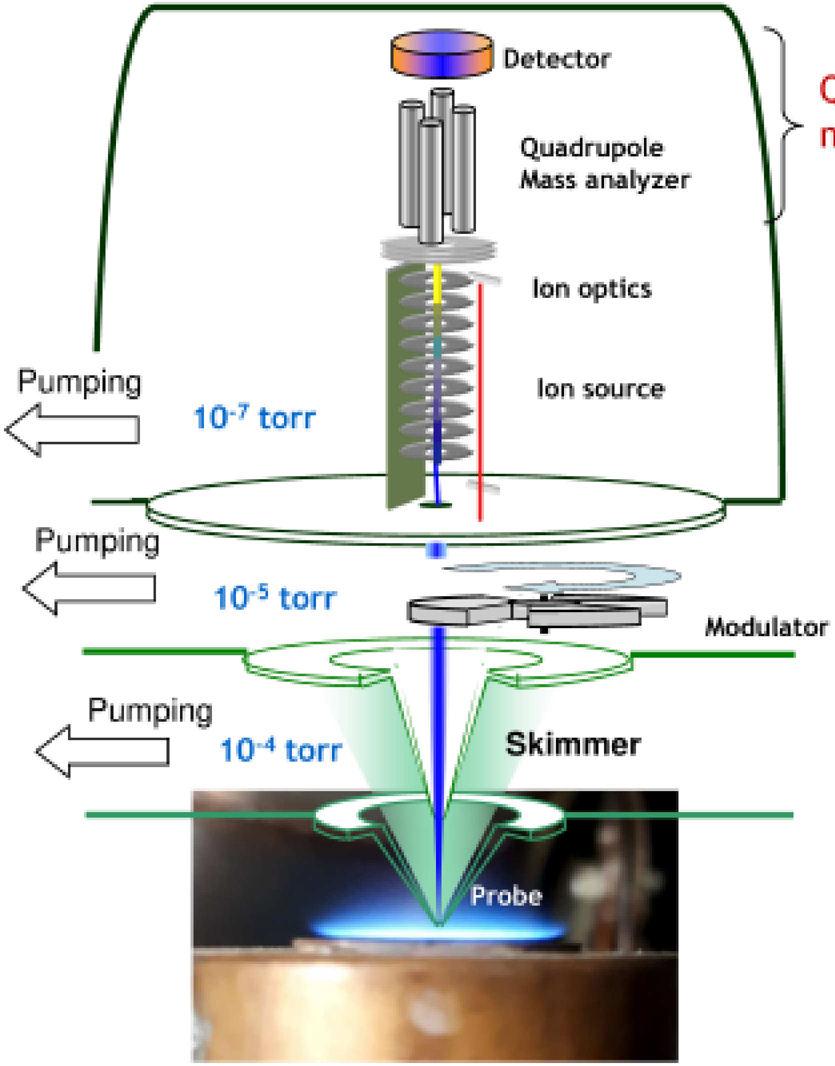
-New experimental data on the flame structure of $NH_3/H_2/O_2/Ar$(φ=0.8, 1.0 и 1.2) at 4 and 6 atm

-The comparison of the experiments with 8 published detailed chemical kinetic models of ammonia oxidation

-The analysis of the equivalence ratio and pressure effect on NOx formation

Experiment

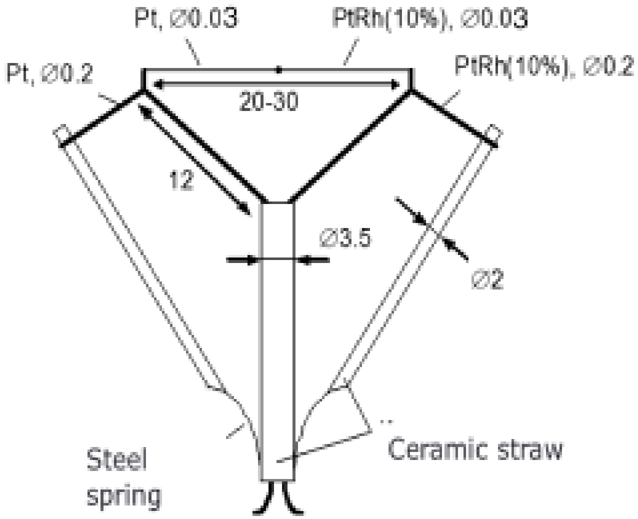
The measurement of species concentration Molecular-beam mass spectrometry



Quadrupole mass spectrometer

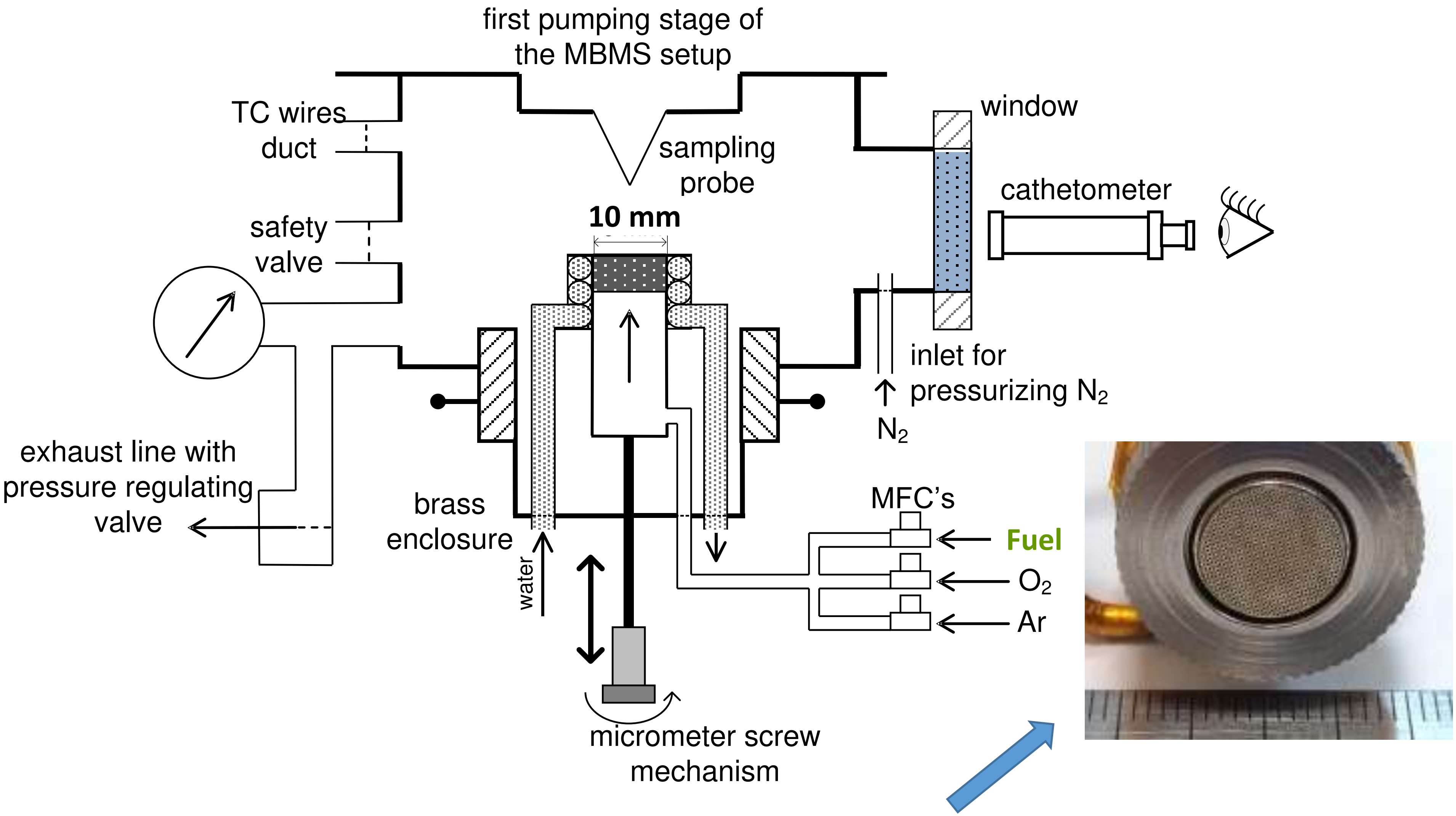
«Soft» electron impact ionization ±0.25 eV

Temperature measurement: microthermocouple technique



Experiment

High pressure chamber



Holes diameter- 0.2 mm, distance between the holes centers– 0.28 mm, thickness of the disc – 1.5 mm. Material – brass, galvanic coating- Ni (0.02 mm)

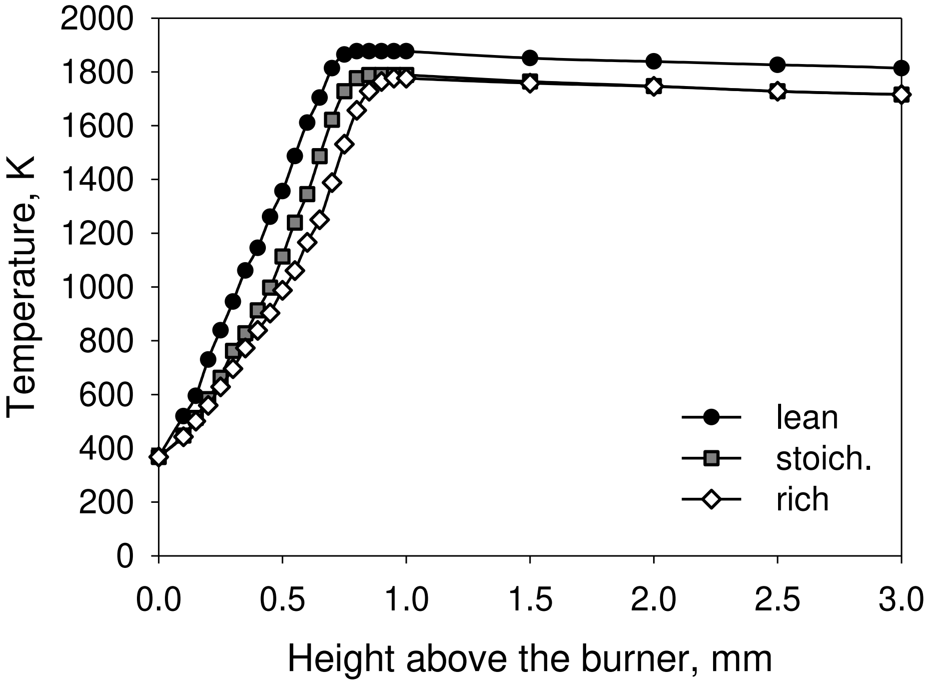
Modeling

For numerical simulations PREMIX code from CHEMKIN package was used

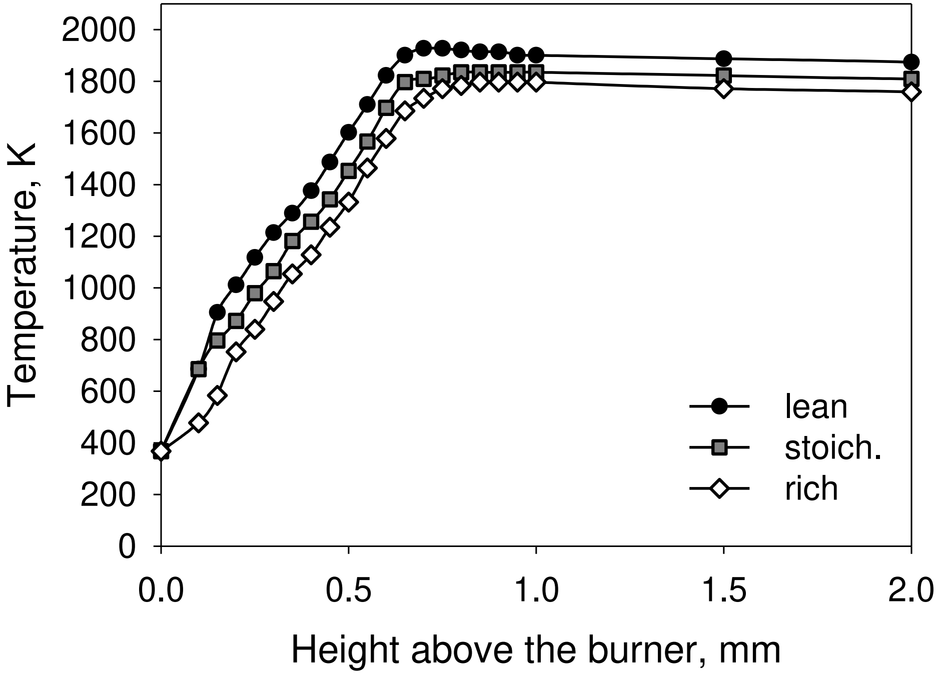
Name on graphs	*Reactions/species number*	*Year*	*Reference*
Model 1	***151 / 1397***	2018	*P. Glarborg et al. Prog. Energy Combust. Sci. 2018, 67, 31–68*
Model 2	***59 / 365***	2018	*E.C. Okafor et al. Combust. Flame 2018, 187, 185–198*
Model 3	***127 / 1207***	2010	*F.H.V. Coppens et al. Combust. Flame 2007, 149 (4), 409–417*
Model 4	***38 / 263***	2021	*X. Zhang et al. Combust Flame 2021, 234, 111653*
Model 5	***40 / 257***	2021	*B. Mei et al. Combust. Flame 2021, 231, 111472*
Model 6	***31 / 203***	2021	*A. Bertolino et al. Combust. Flame 2021, 229, 111366.*
Model 7	***125 / 1099***	2021	*K.P. Shrestha et al. Proc. Combust. Inst 2021, 38, 2163–2174*
Model 8	***36 / 298***	2021	*X. Han et al. Combust. Flame 2021, 228, 13–28.*

Results: temperature profiles

Temperature profiles in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at 4 and 6 atm



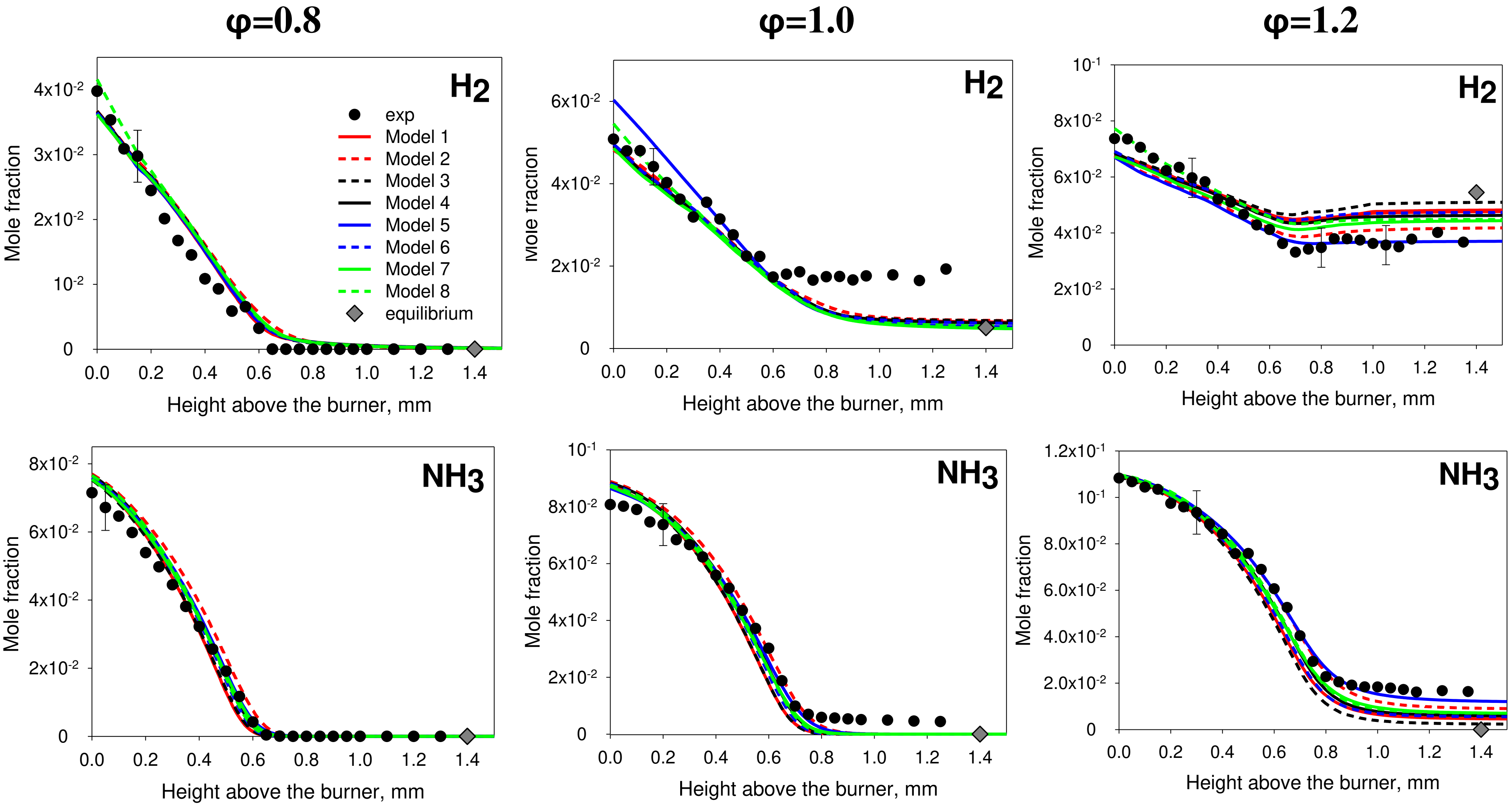
P=4 atm.



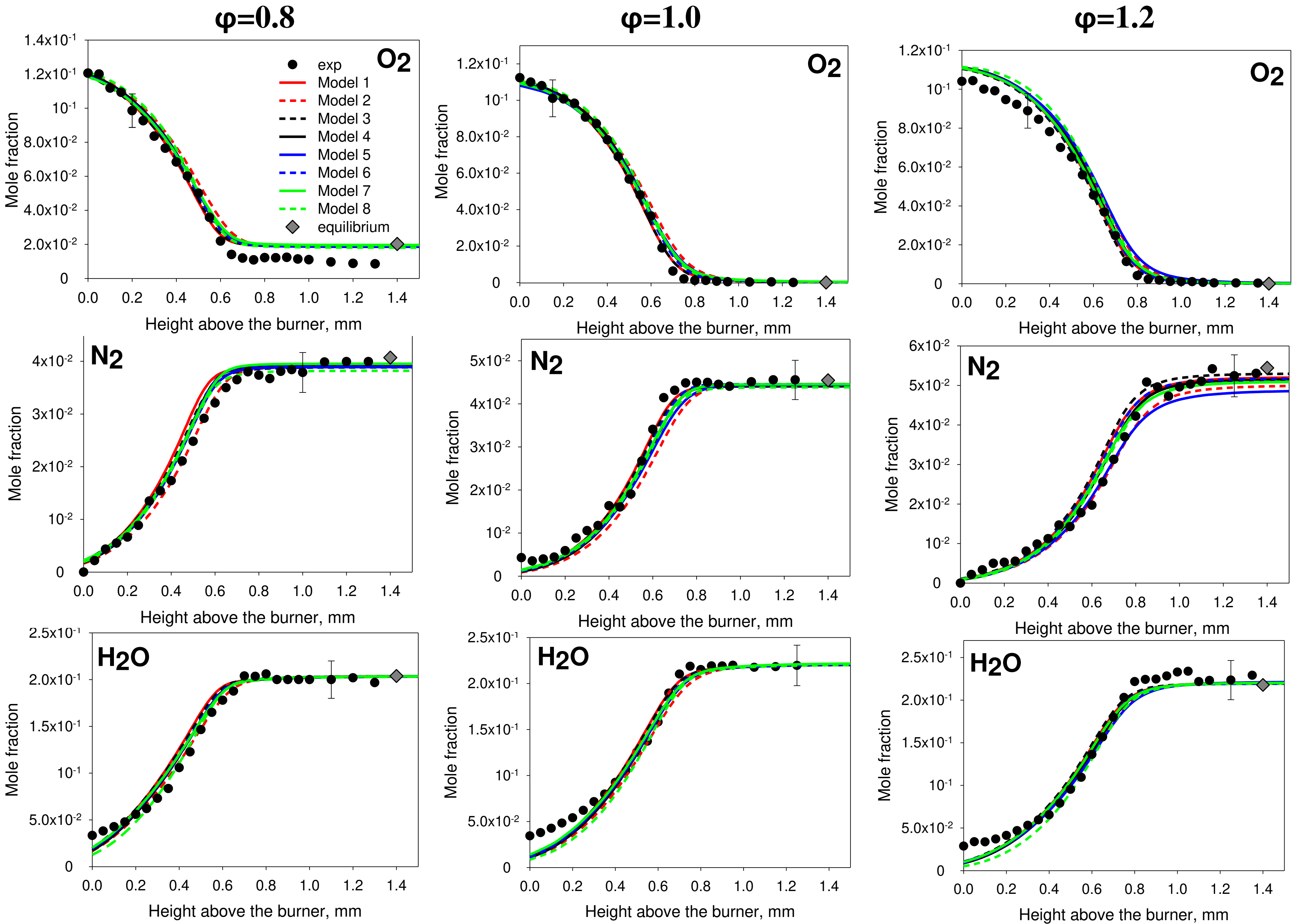
P=6 atm.

Results: flame structure at 4 atm

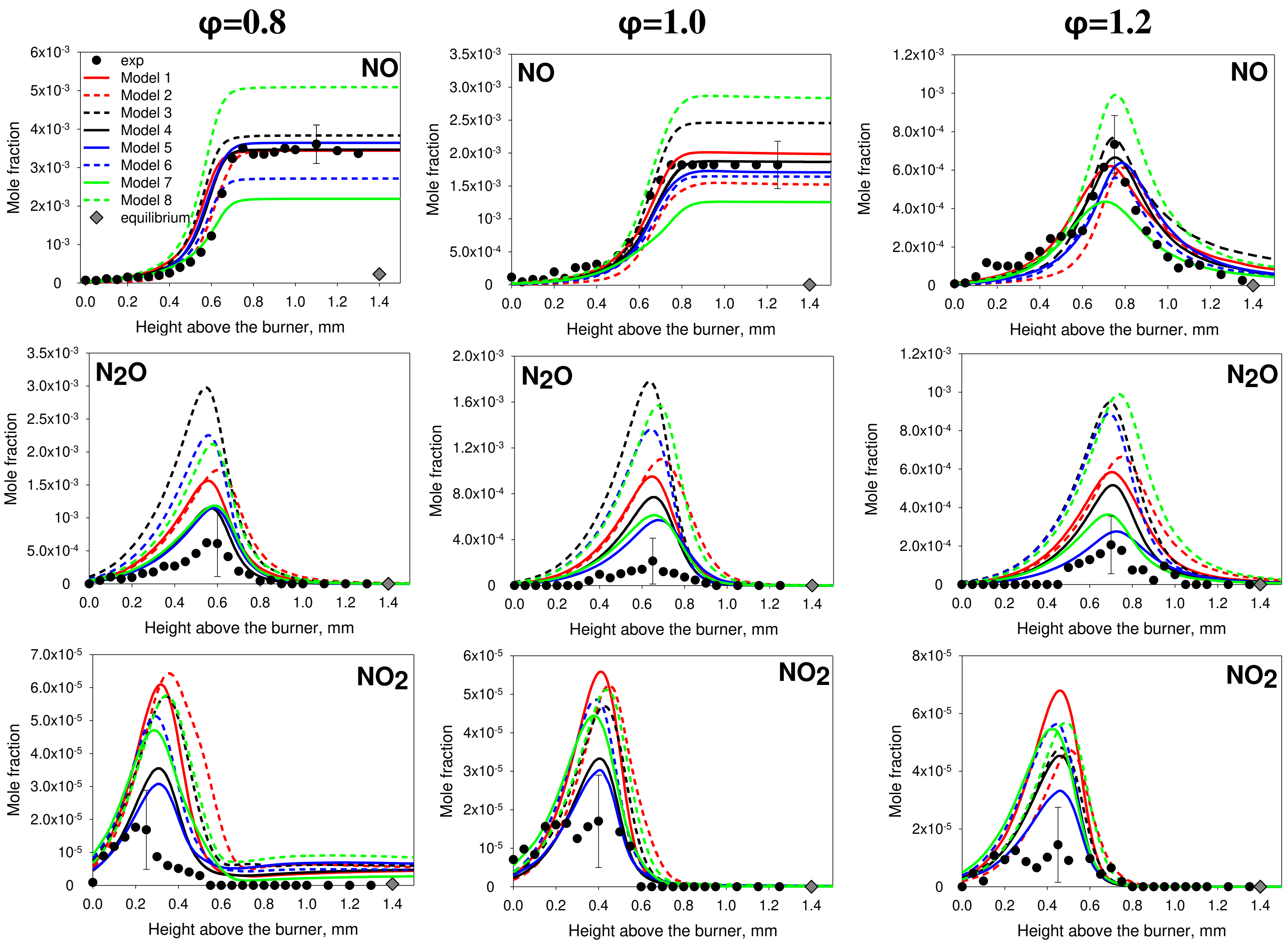
Concentration profiles of H_2 and NH_3 in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=4 atm



Concentration profiles of O_2, N_2 and H_2O in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=4 atm



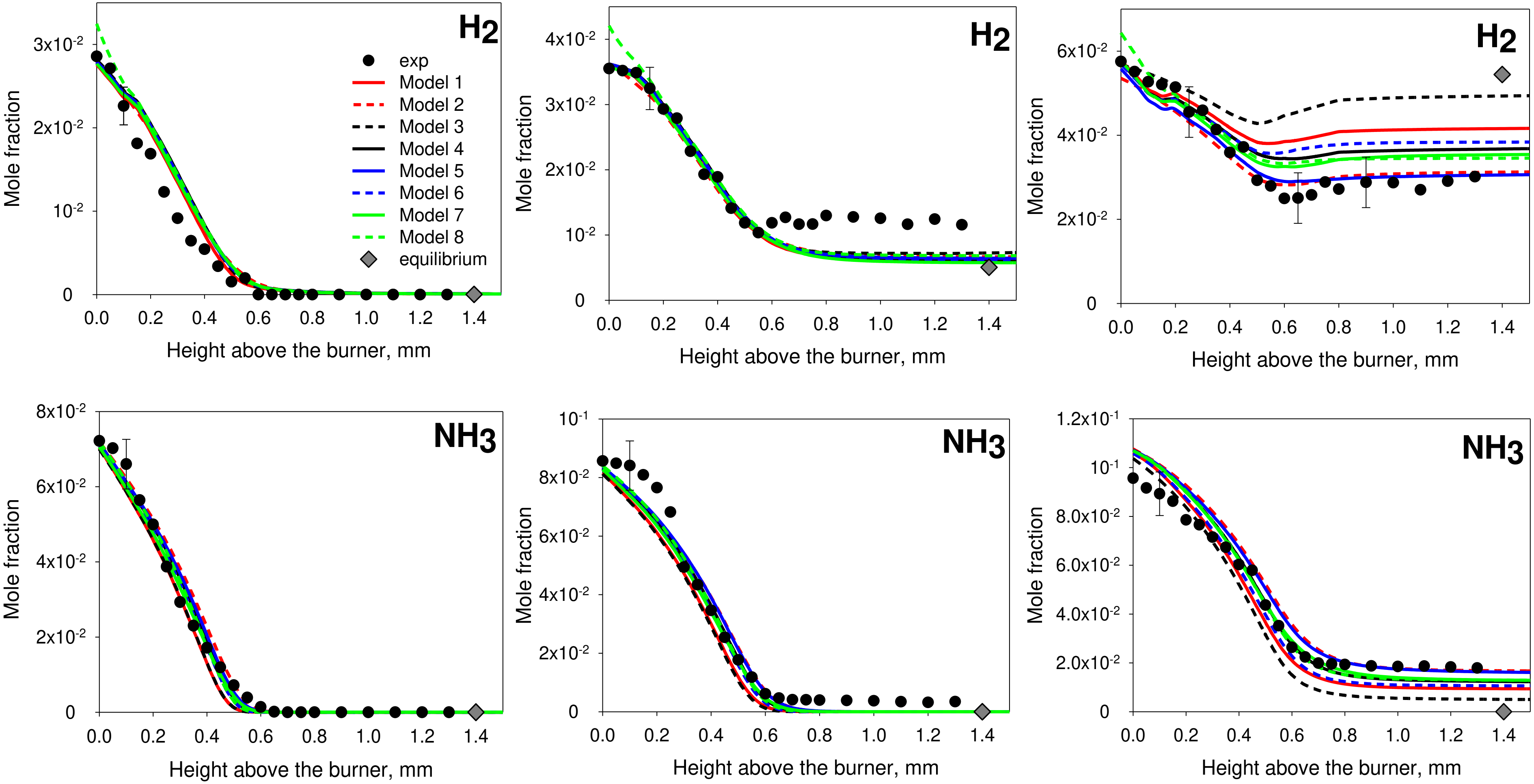
Concentration profiles of NO, N_2O and NO_2 in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=4 atm



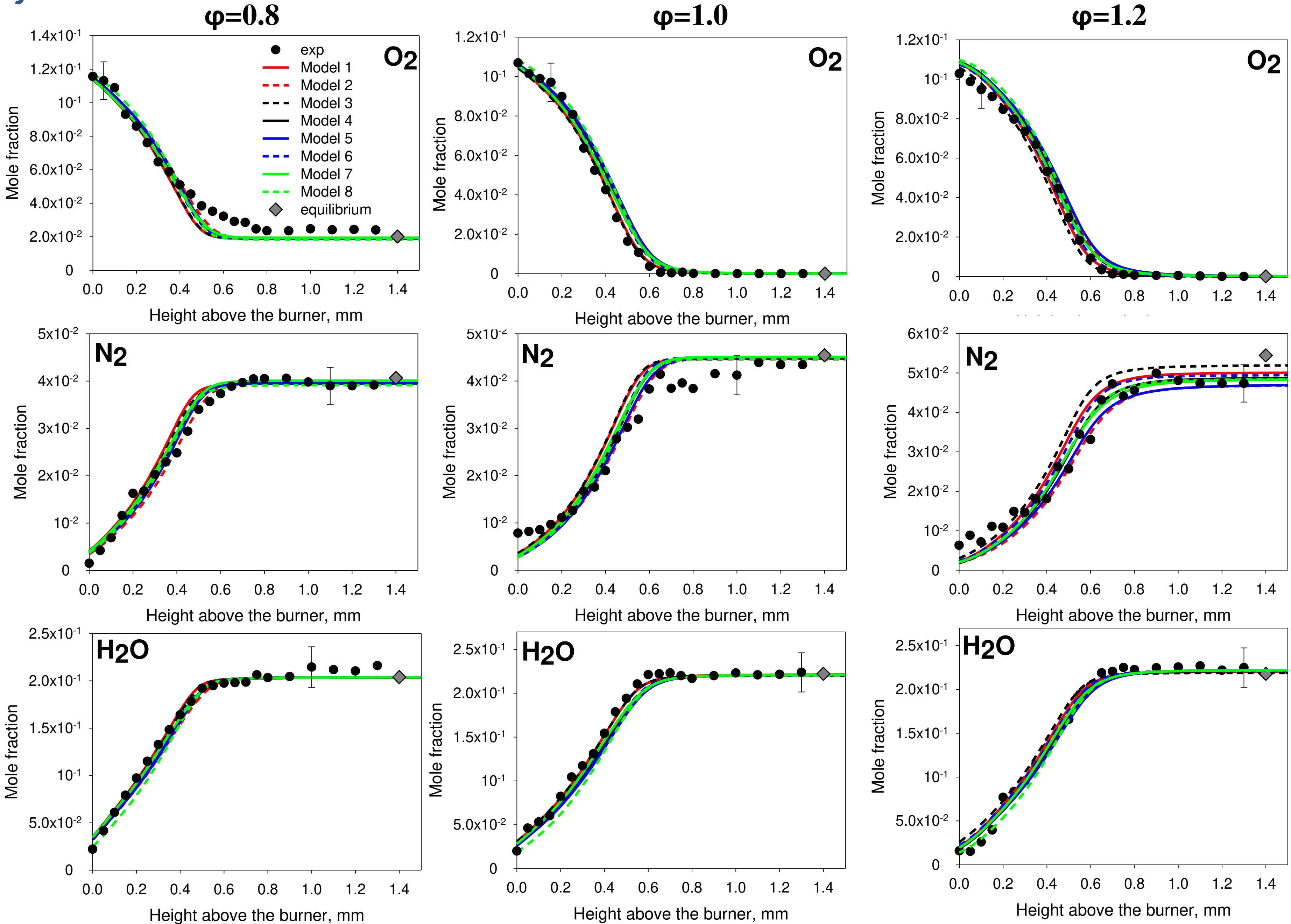
Results: flame structure at 6 atm

Concentration profiles of H_2 and NH_3 in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=6 atm

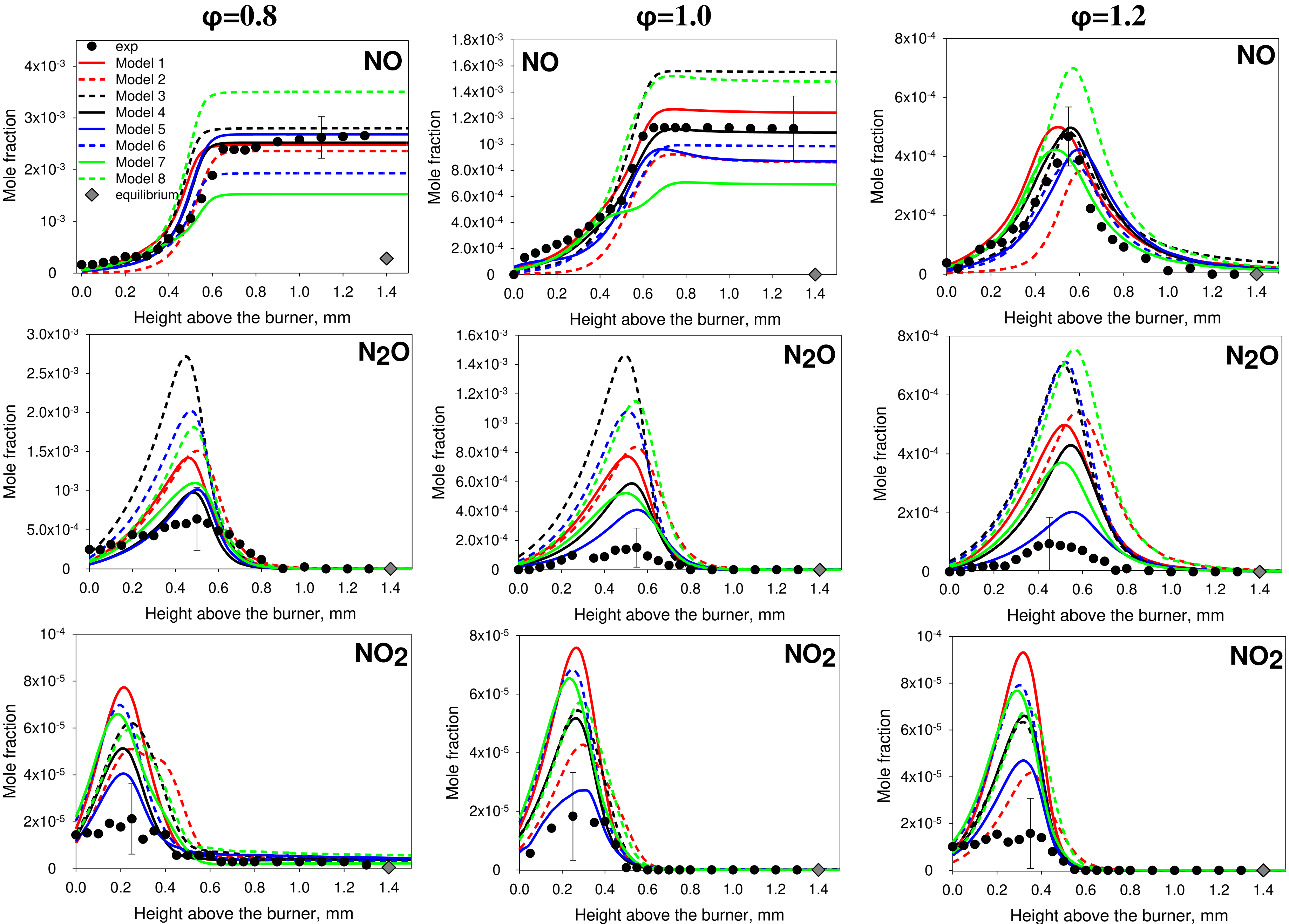
φ=0.8 **φ=1.0** **φ=1.2**



Concentration profiles of O_2, N_2 and H_2O in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=6 atm

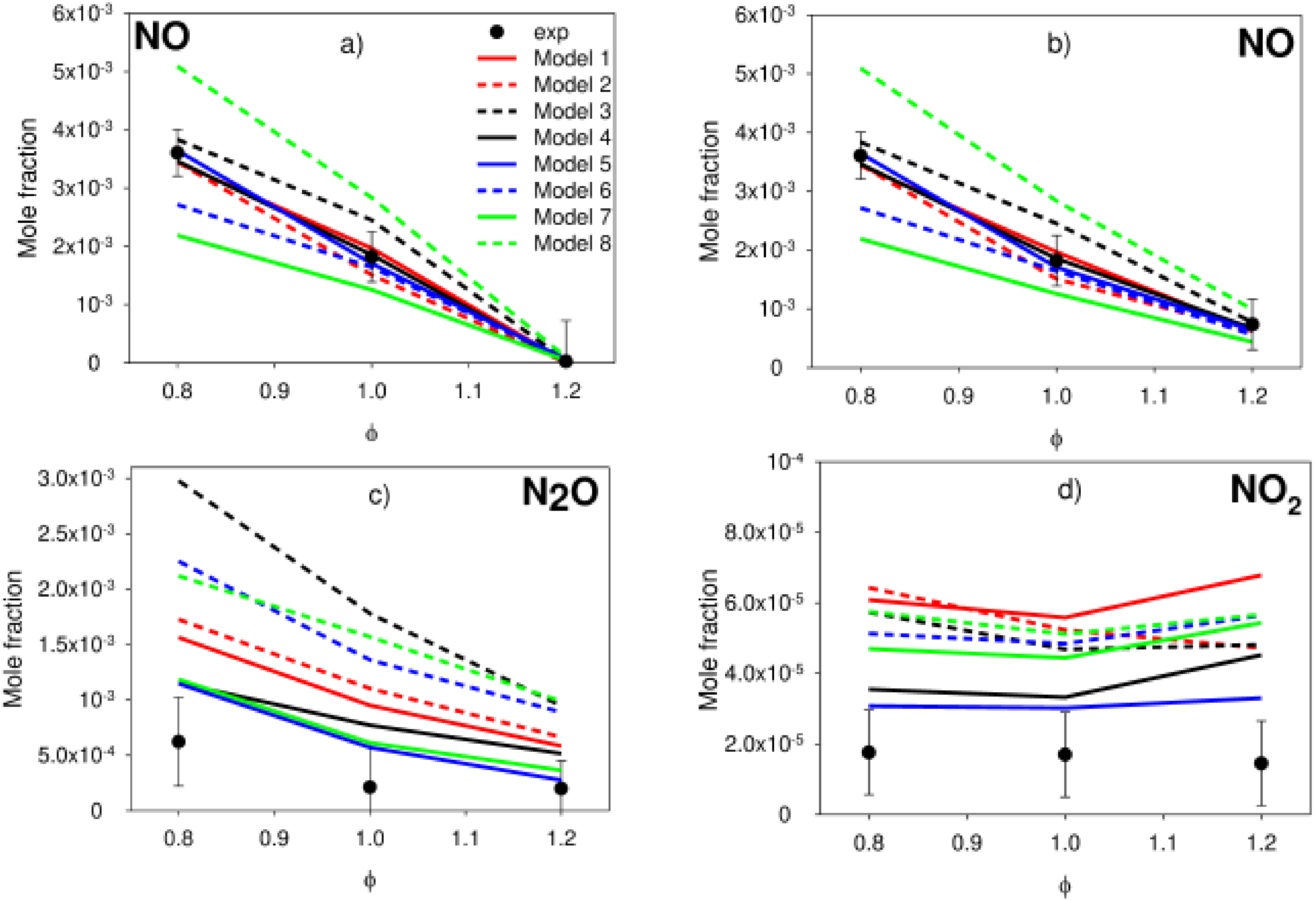


Concentration profiles of NO, N_2O and NO_2 in lean, stoichiometric and rich $NH_3/H_2/O_2/Ar$ flames at P=6 atm

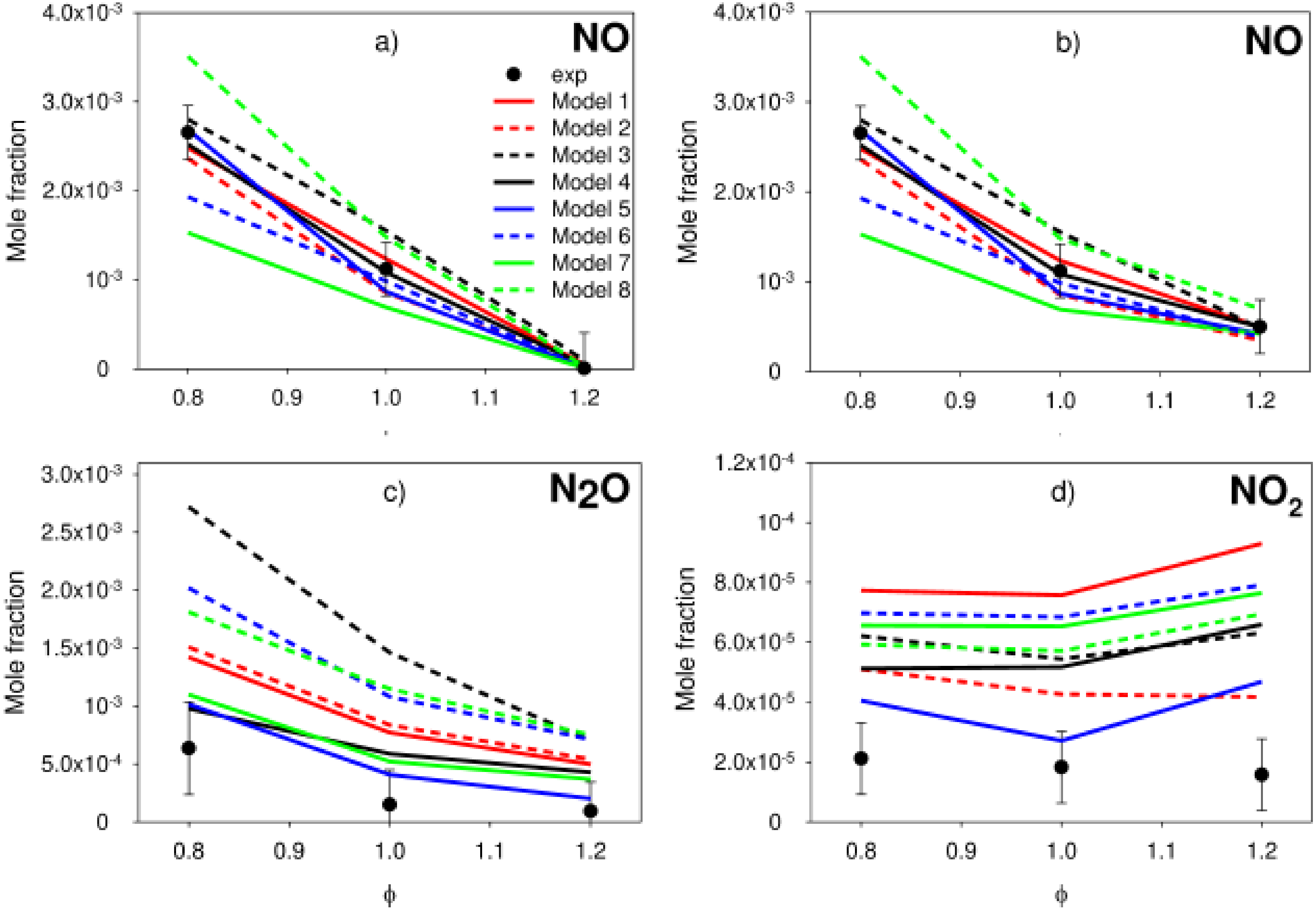


NOx formation: effect of φ

NO vs φ in the post flame zone(a) and the maximum concentration of NO (b), N_2O (c) and NO_2 (d) in $NH_3/H_2/O_2/Ar$ flames at P=4 atm.

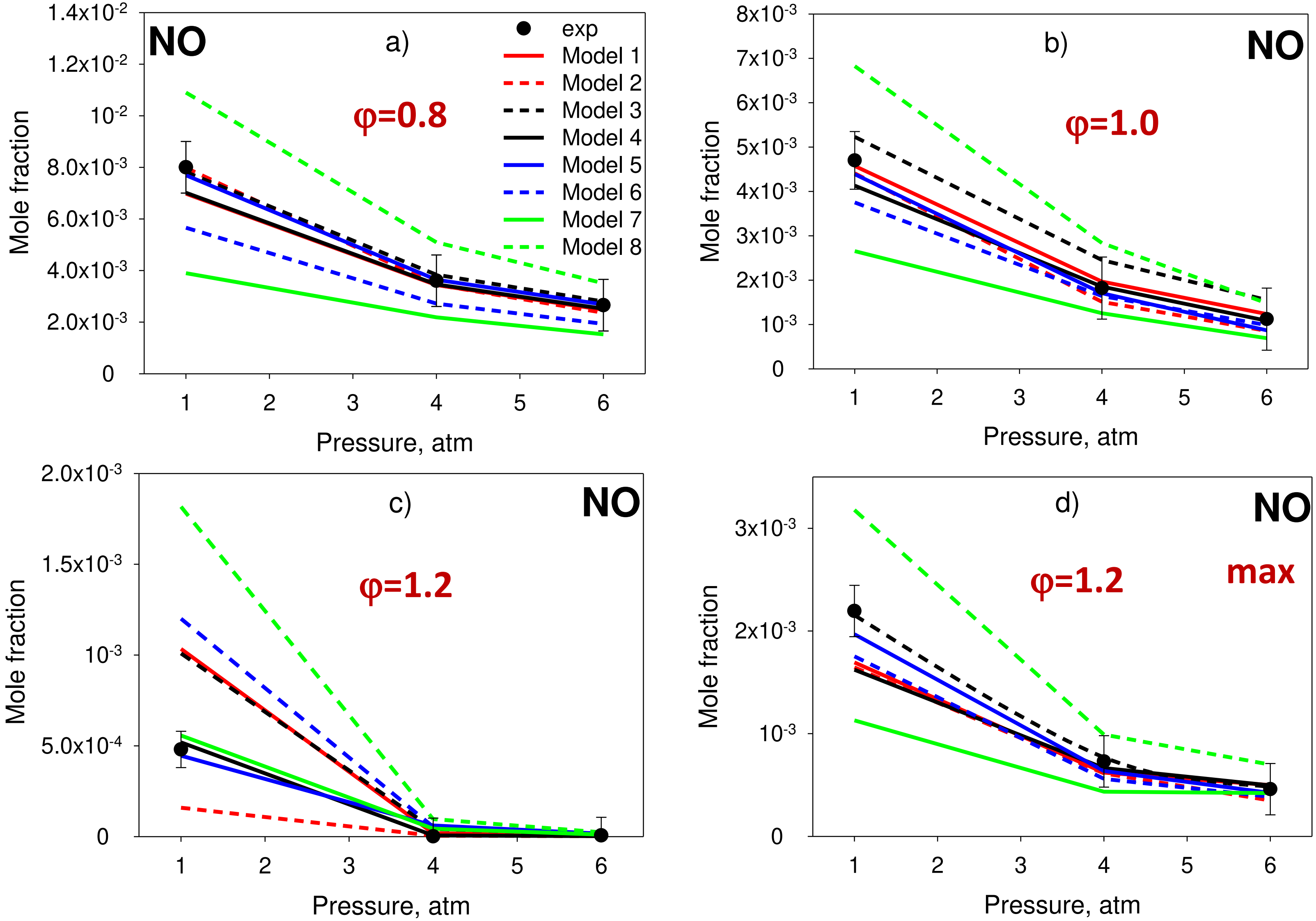


NO vs φ in the post flame zone(a) and the maximum concentration of NO (b), N_2O (c) u NO_2 (d) in $NH_3/H_2/O_2/Ar$ flames at P=6 atm.



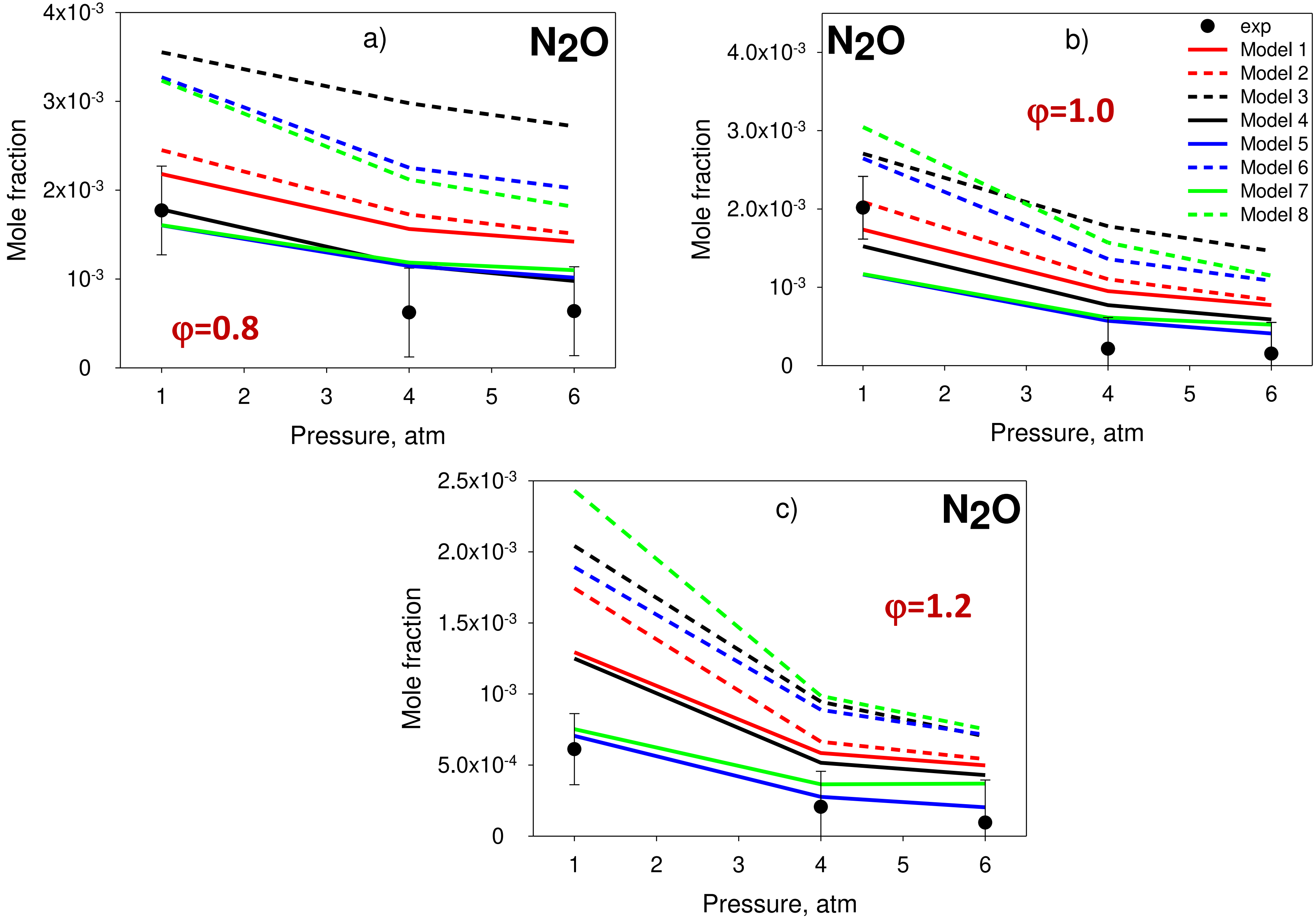
NOx formation: effect of P

NO concentration in the post-flame zone in lean (a), stoichiometric (b) and rich (c) flames and NO maximum concentration in rich flame vs P



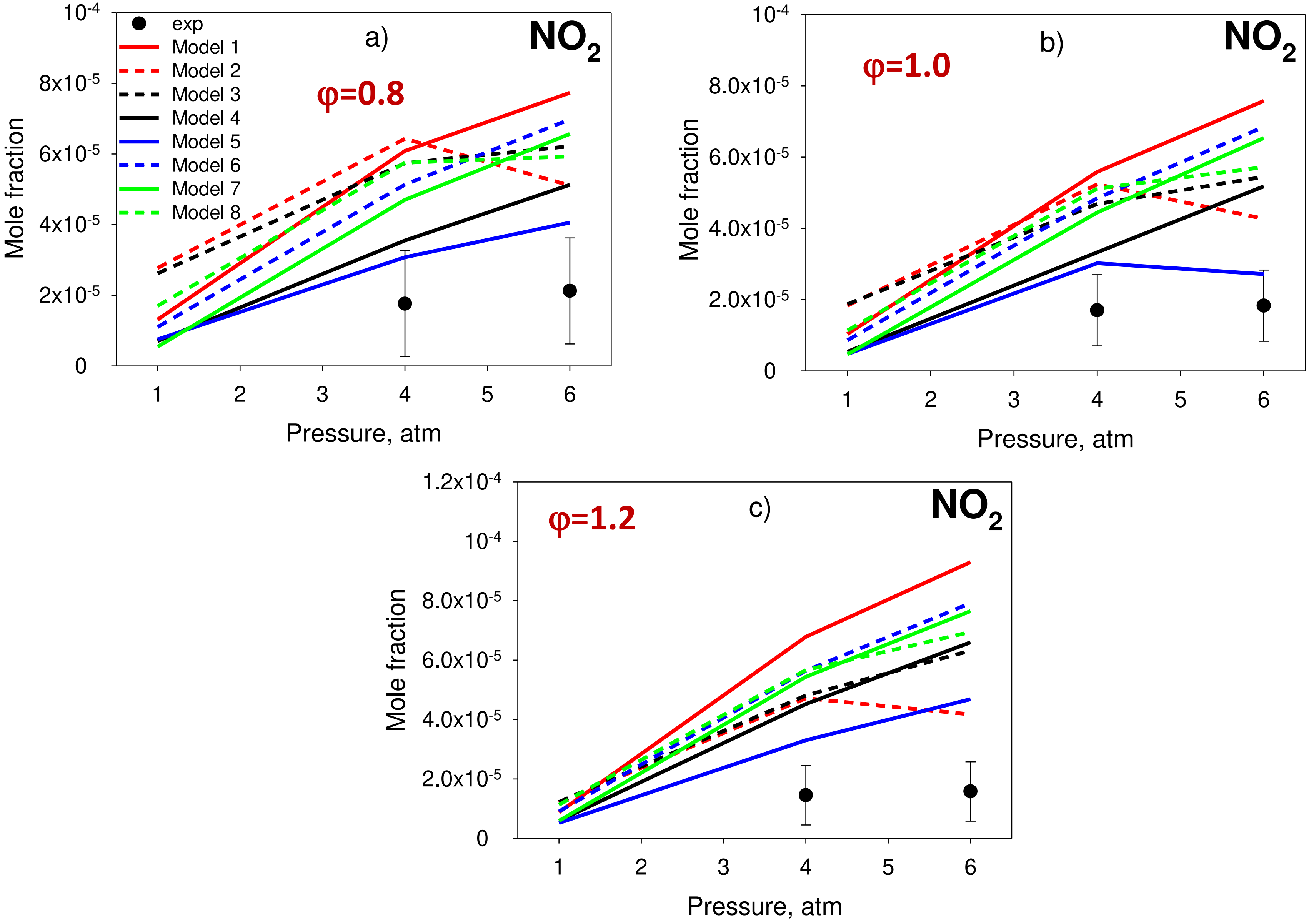
Experimental data at 1 atm: *K.N. Osipova et al. Int. J. Hydrog. Energy, 2021, 46, 39942–39954.*

N_2O maximum concentration in lean (a), stoichiometric (b) and rich (c) flames vs P

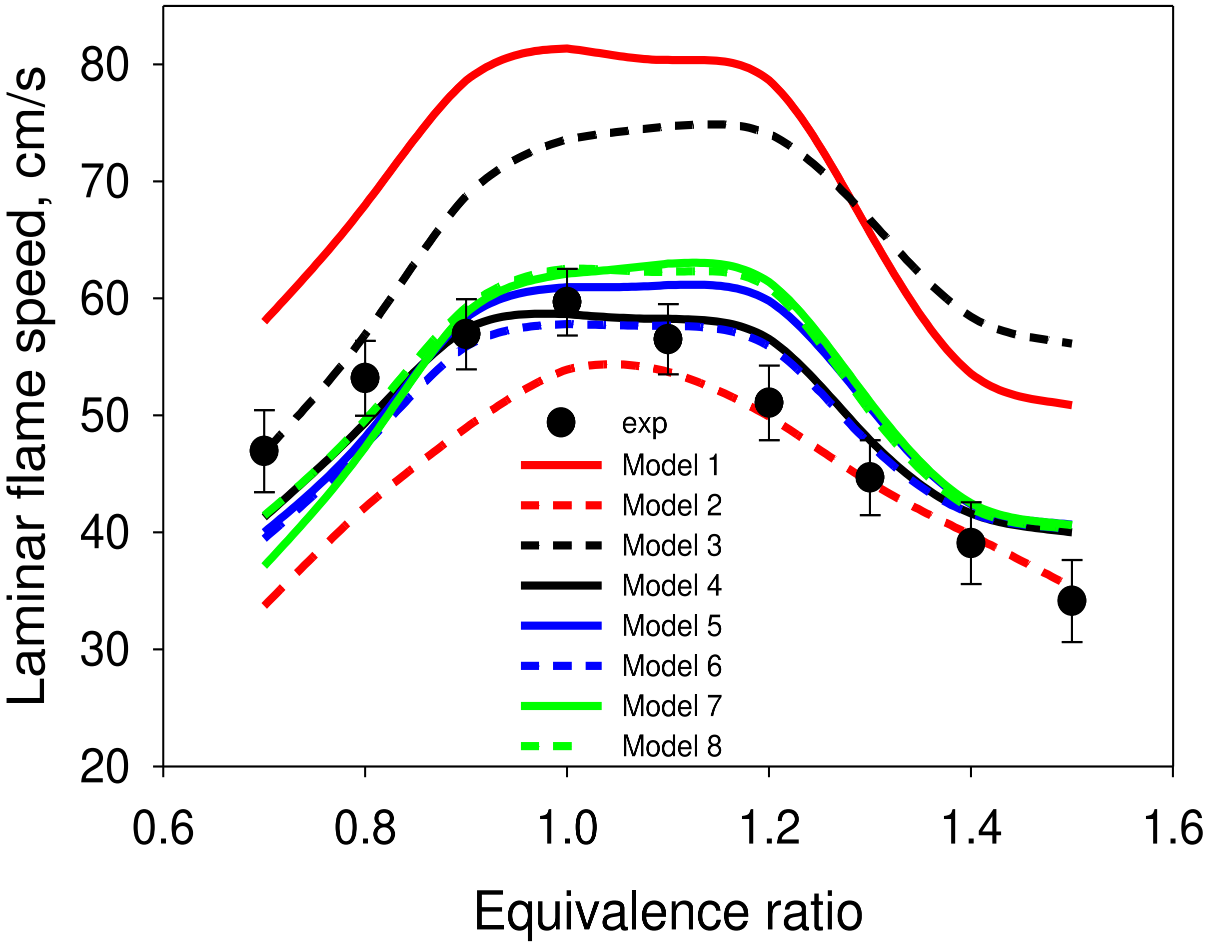


Experimental data at 1 atm: *K.N. Osipova et al. Int. J. Hydrog. Energy, 2021, 46, 39942–39954.*

NO_2 maximum concentration in lean (a), stoichiometric (b) and rich (c) flames vs P



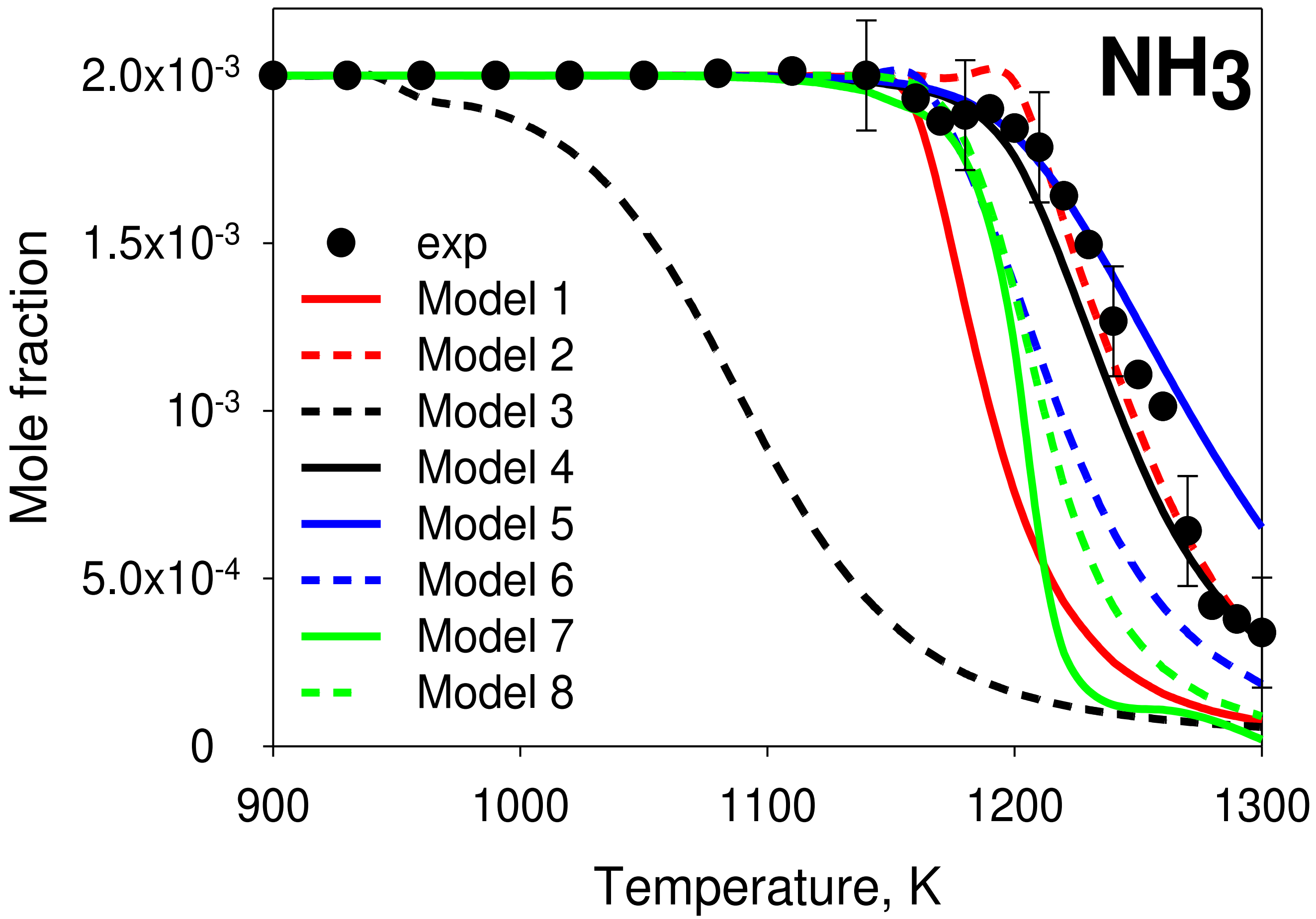
Laminar burning velocity of $NH_3/H_2/O_2/N_2$ flames



$NH_3/H_2=7/3$, $N_2/O_2=7/3$, $T_0=368K$

Experimental data: *K.N. Osipova et al. Int. J. Hydrog. Energy, 2021, 46, 39942–39954.*

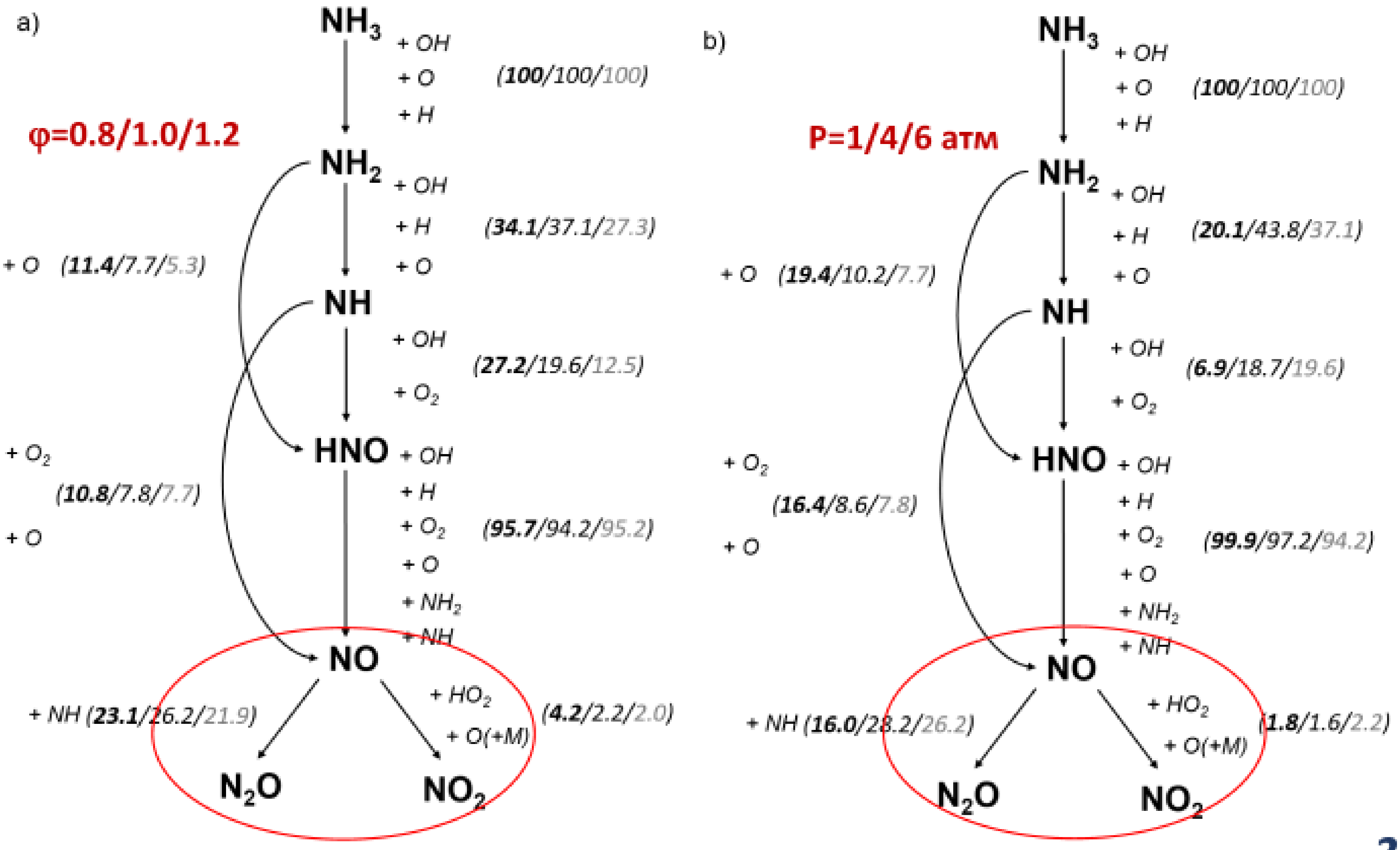
Oxidation of $NH_3/H_2/O_2/Ar$ blend in JSR



NH_3/H_2=7/3, NH_3=2000ppm, τ=1 s, p=1 atm

Experimental data: *K.N. Osipova et al. Fuel, 2022, 310, 122202.*

The pathways of N_2O u NO_2 formation from ammonia molecule



a)

φ=0.8/1.0/1.2

NH_3 + OH + O + H (**100**/100/100)

NH_2 + OH + H + O (**34.1**/37.1/27.3)

+ O (**11.4**/7.7/5.3)

NH + OH + O_2 (**27.2**/19.6/12.5)

+ O_2 (**10.8**/7.8/7.7) + O

HNO + OH + H + O_2 + O + NH_2 + NH (**95.7**/94.2/95.2)

NO

+ NH (**23.1**/26.2/21.9)

+ HO_2 + O(+M) (**4.2**/2.2/2.0)

N_2O

NO_2

b)

P=1/4/6 атм

NH_3 + OH + O + H (**100**/100/100)

NH_2 + OH + H + O (**20.1**/43.8/37.1)

+ O (**19.4**/10.2/7.7)

NH + OH + O_2 (**6.9**/18.7/19.6)

+ O_2 (**16.4**/8.6/7.8) + O

HNO + OH + H + O_2 + O + NH_2 + NH (**99.9**/97.2/94.2)

NO

+ NH (**16.0**/28.2/26.2)

+ HO_2 + O(+M) (**1.8**/1.6/2.2)

N_2O

NO_2

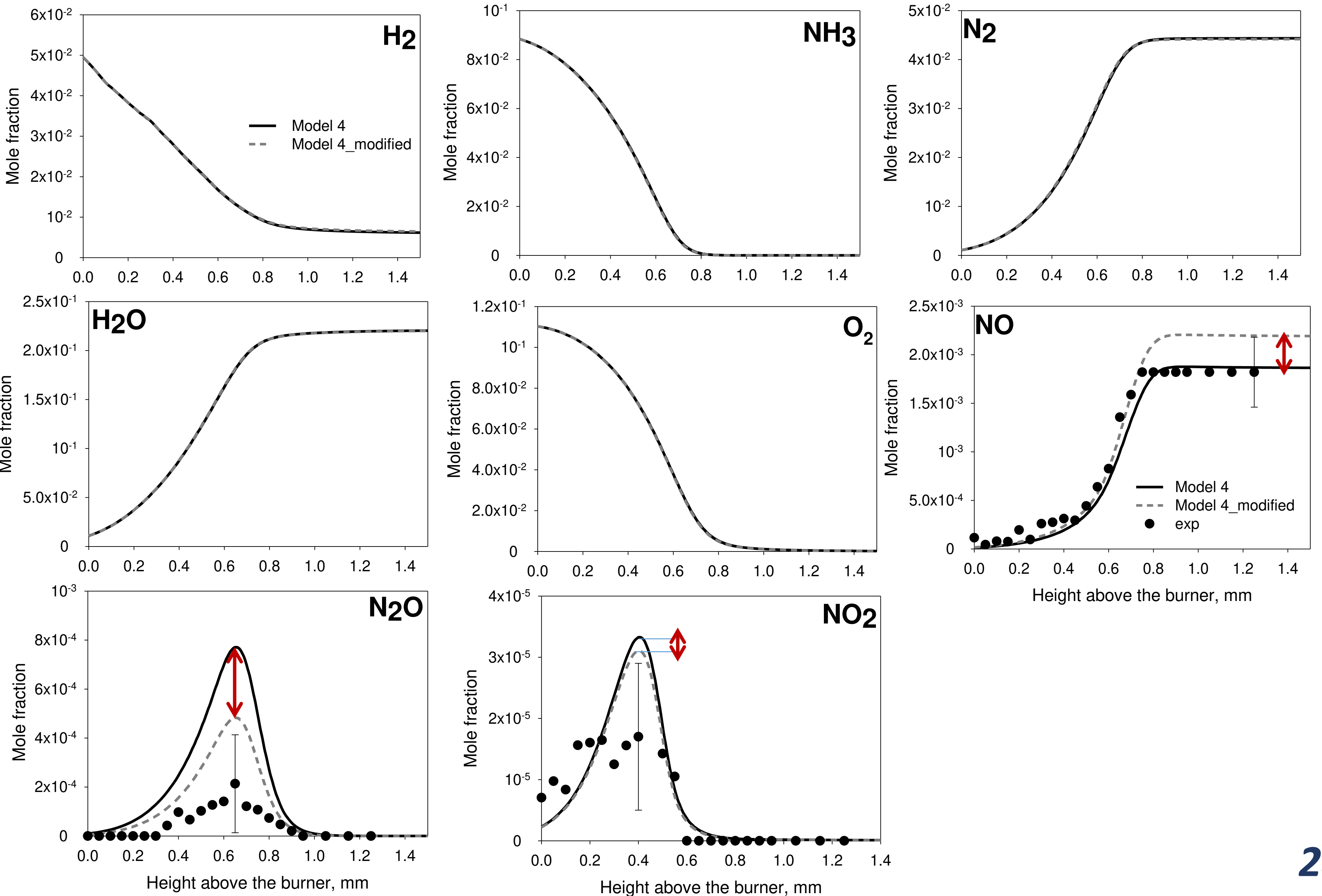
The modification of Model 4 for better agreement of N_2O and NO_2 concentration profiles with experimental results

$$k=A\cdot T^{n}\cdot \exp(-E_a/RT)$$

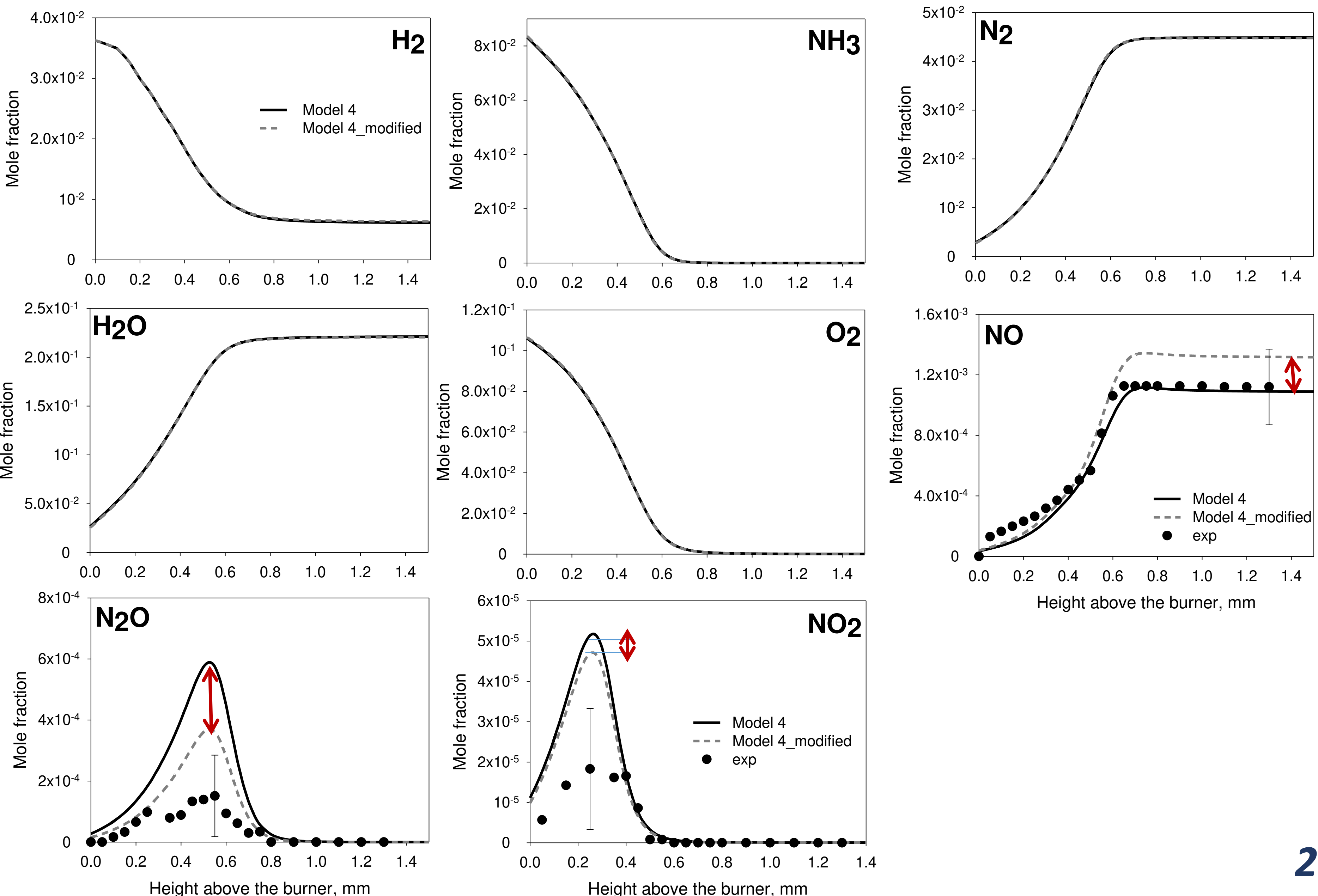
Reaction	Rate constant modification*
$NO+NH=N_2O+H$	A`=A/2
$NO+HO_2=NO_2+OH$	A`=A/1.4
$NO+O(+M)=NO_2(+M)$	A`=A/2

** Within the recommended limits [D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker, J. Warnatz, Evaluated Kinetic Data for Combustion Modeling: Supplement II, J. Phys. Chem. Ref. Data 34 (2005) 757–1397.]*

Concentration profiles in stoichiometric (φ=1.0) $NH_3/H_2/O_2/Ar$ at P=4 atm– original and modified mechanisms



Concentration profiles in stoichiometric (φ=1.0) $NH_3/H_2/O_2/Ar$ at P=6 atm– original and modified mechanisms



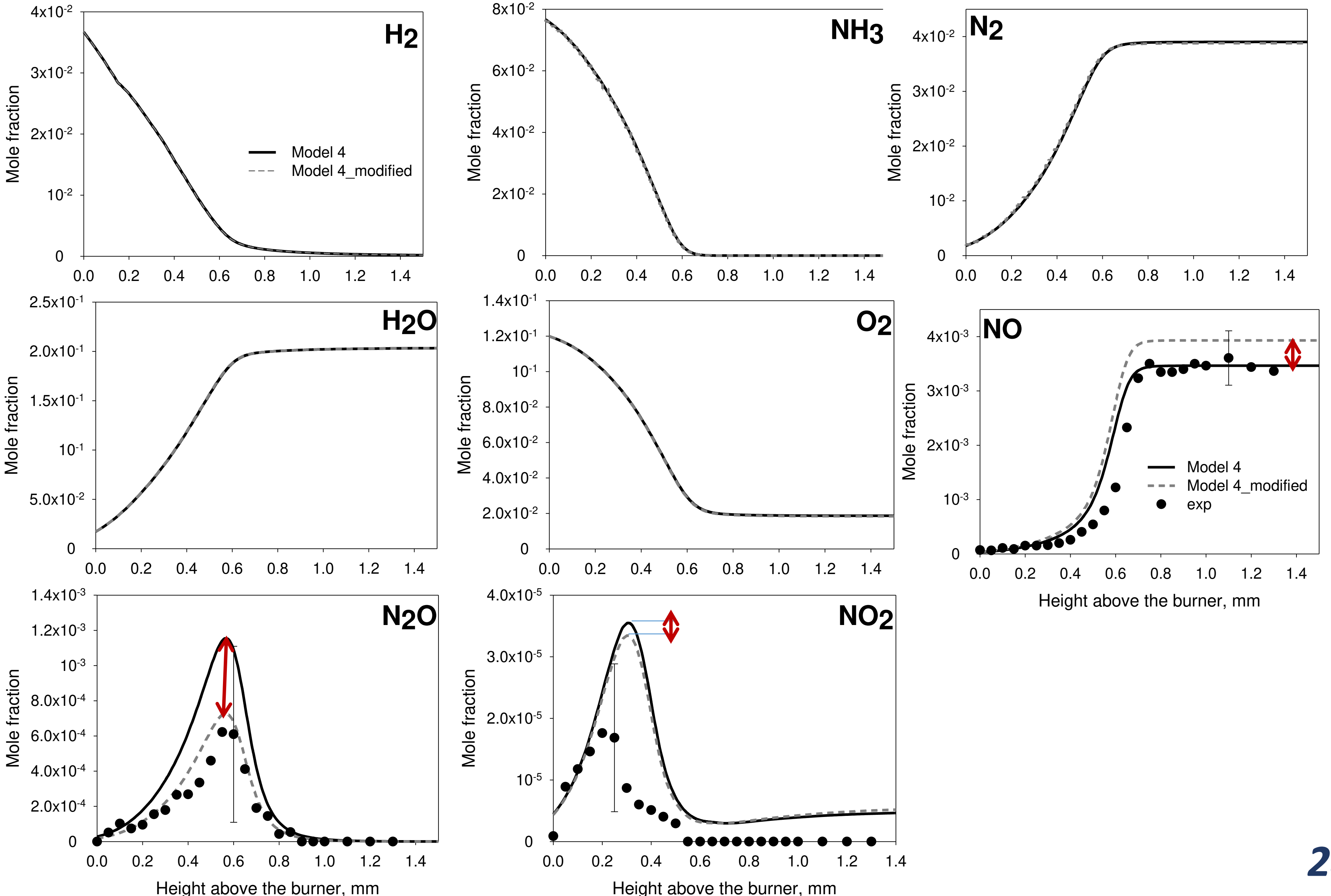
Conclusions

1) Model 4 provided the best agreement between the experimental and numerical data for the large dataset
2) In rich conditions (φ=1.2) NO concentration in the post-flame zone and peak concentrations of NO, N_2O and NO_2 are lower compared to lean and stoichiometric
3) The pressure increase from 1 to 6 atm results into the reduction of NO concentration in the post-flame zone as well as peak concentrations of NO and N_2O
4) Model 4 satisfactorily reproduces the dependence of NO concentration vs P and φ, however, there are larger discrepancies for N_2O and NO_2
5) The reaction pathways analysis indicated that in ammonia/hydrogen flames N_2O and NO_2 mainly form from NO. Therefore, the rate constants of the reactions of N_2O and NO_2 need further refinement.

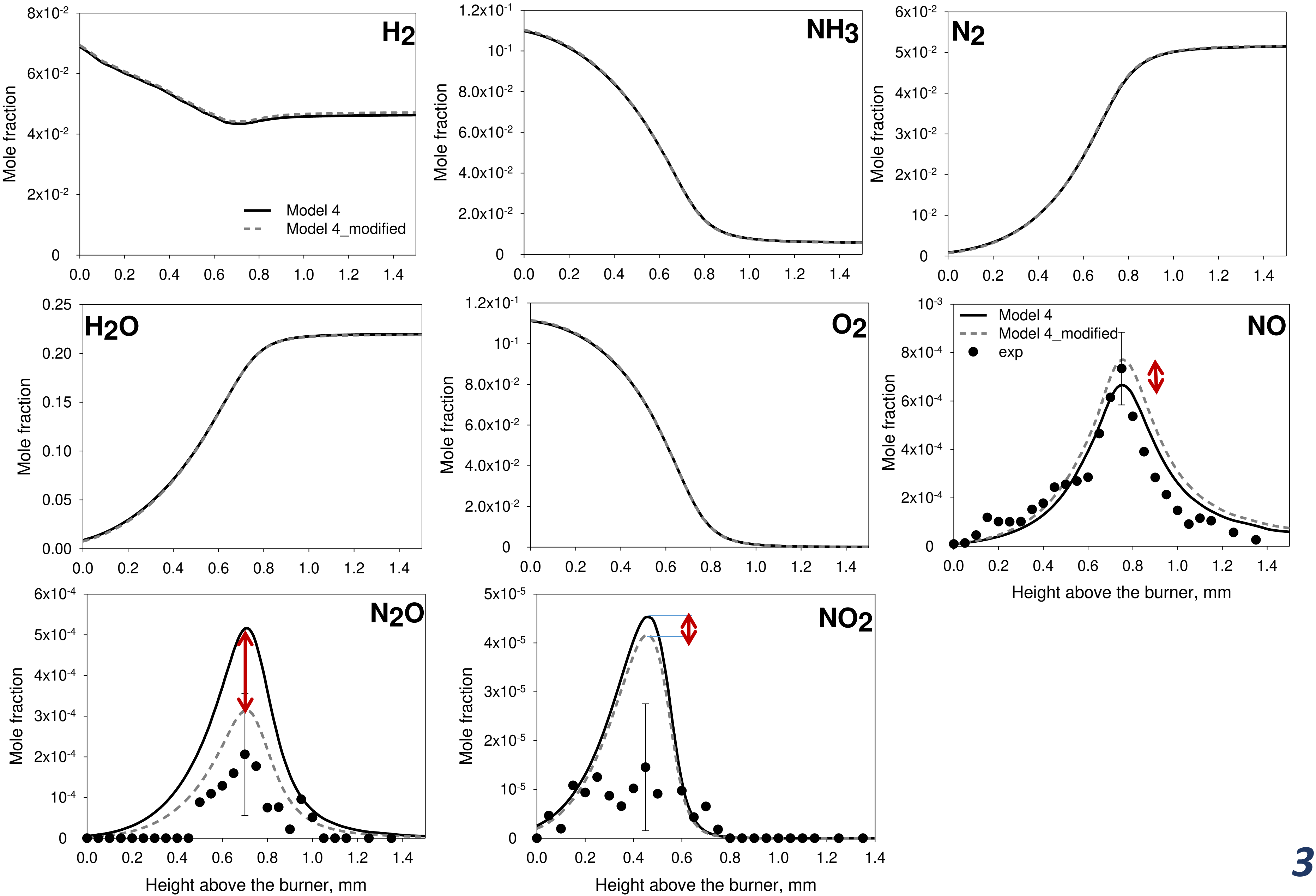
Thank you for your attention!

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Project No: 075-15-2020-806).

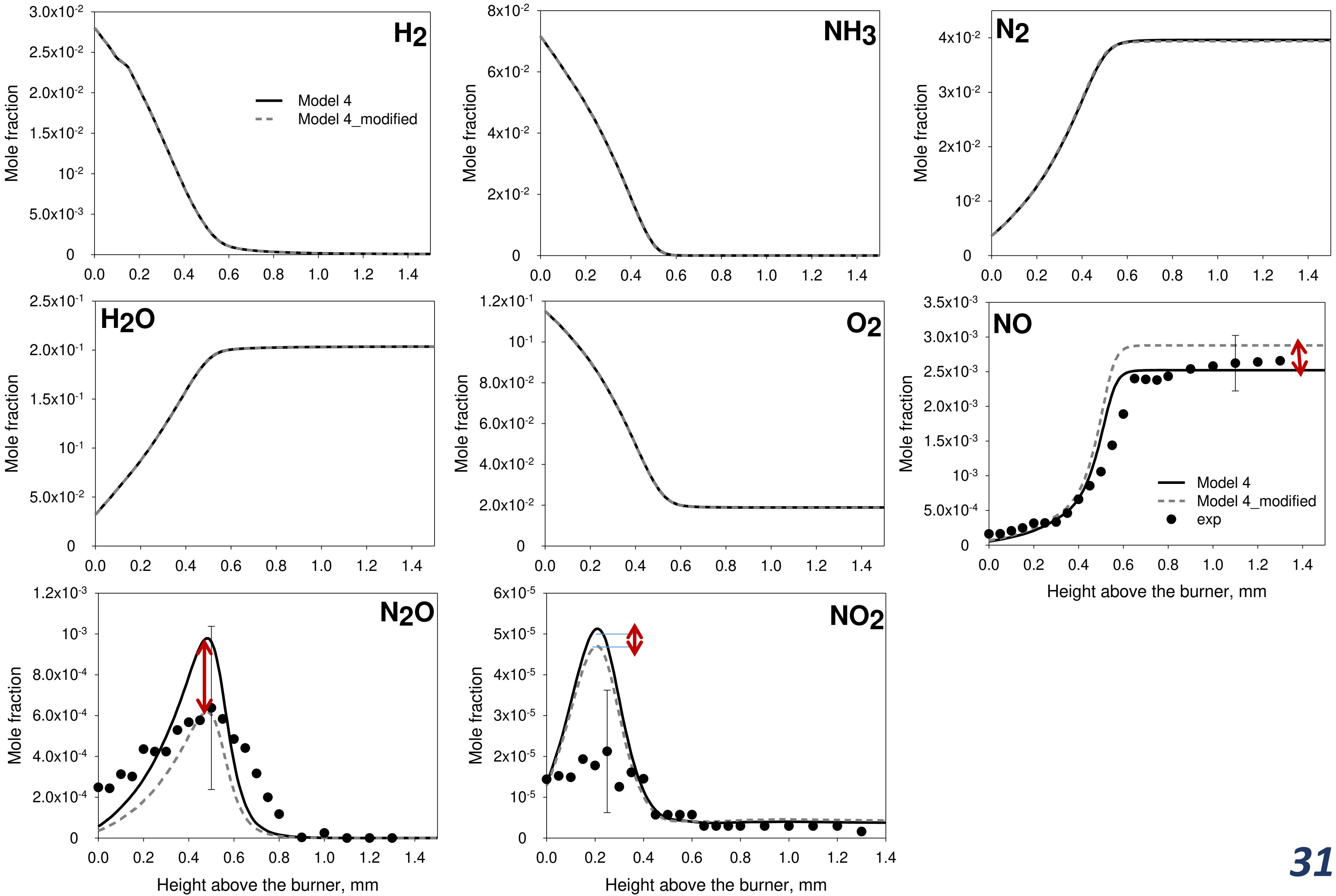
Concentration profiles in lean (φ=0.8) $NH_3/H_2/O_2/Ar$ at P=4 атм – original and modified mechanisms



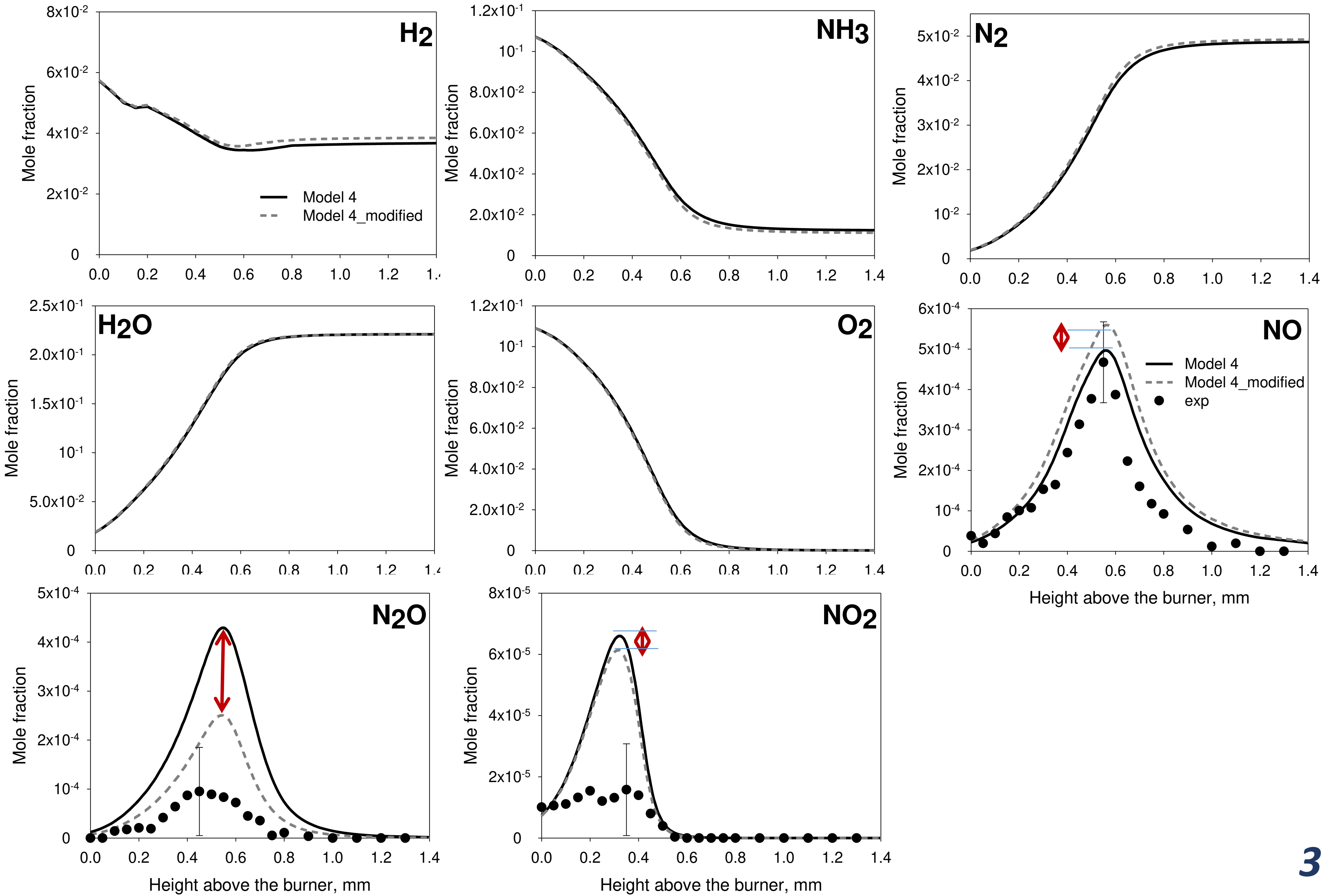
Concentration profiles in rich (φ=1.2) $NH_3/H_2/O_2/Ar$ at P=4 атм – original and modified mechanisms

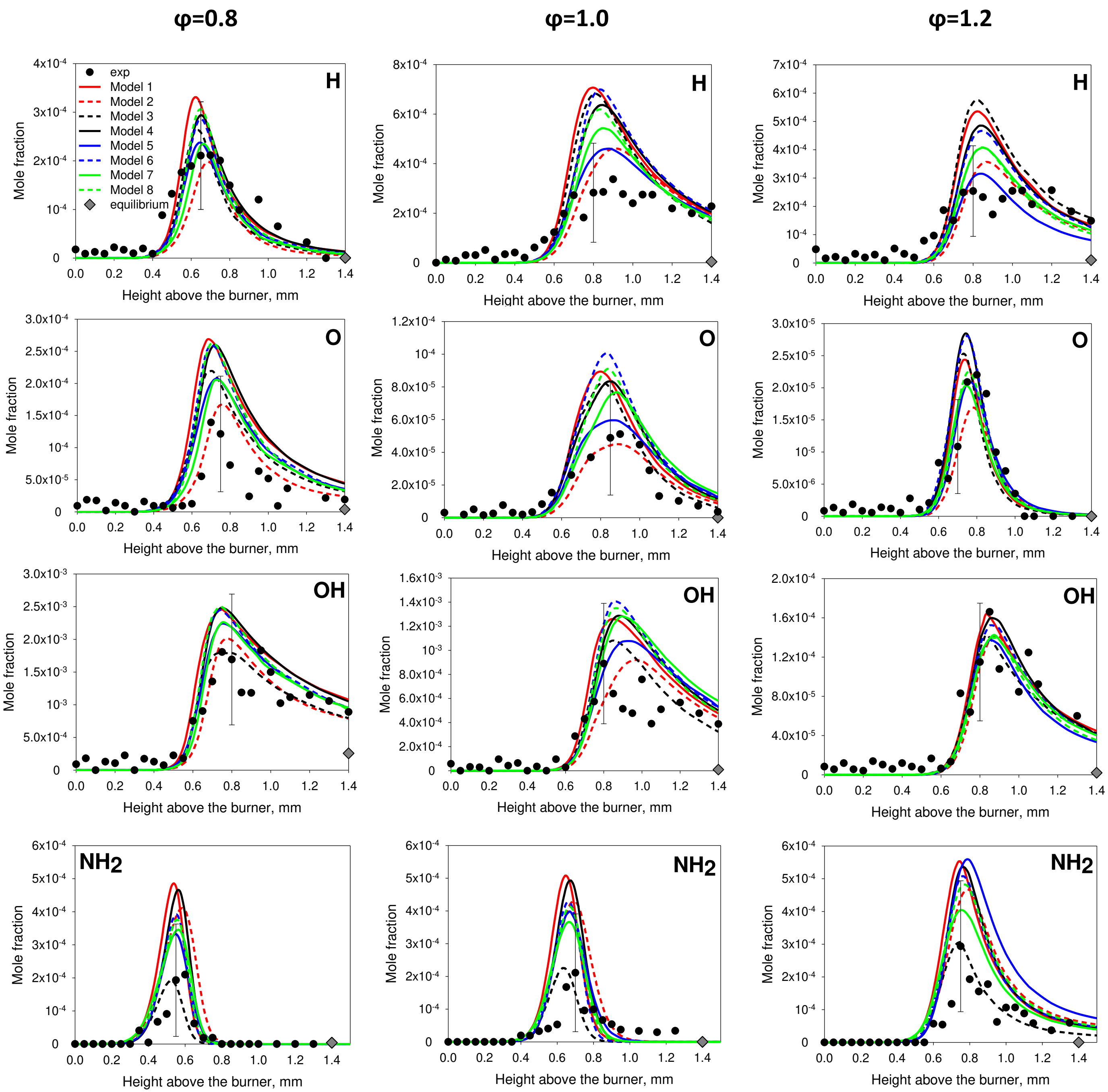


Concentration profiles in lean (φ=0.8) $NH_3/H_2/O_2/Ar$ at P=6 atm – original and modified mechanisms



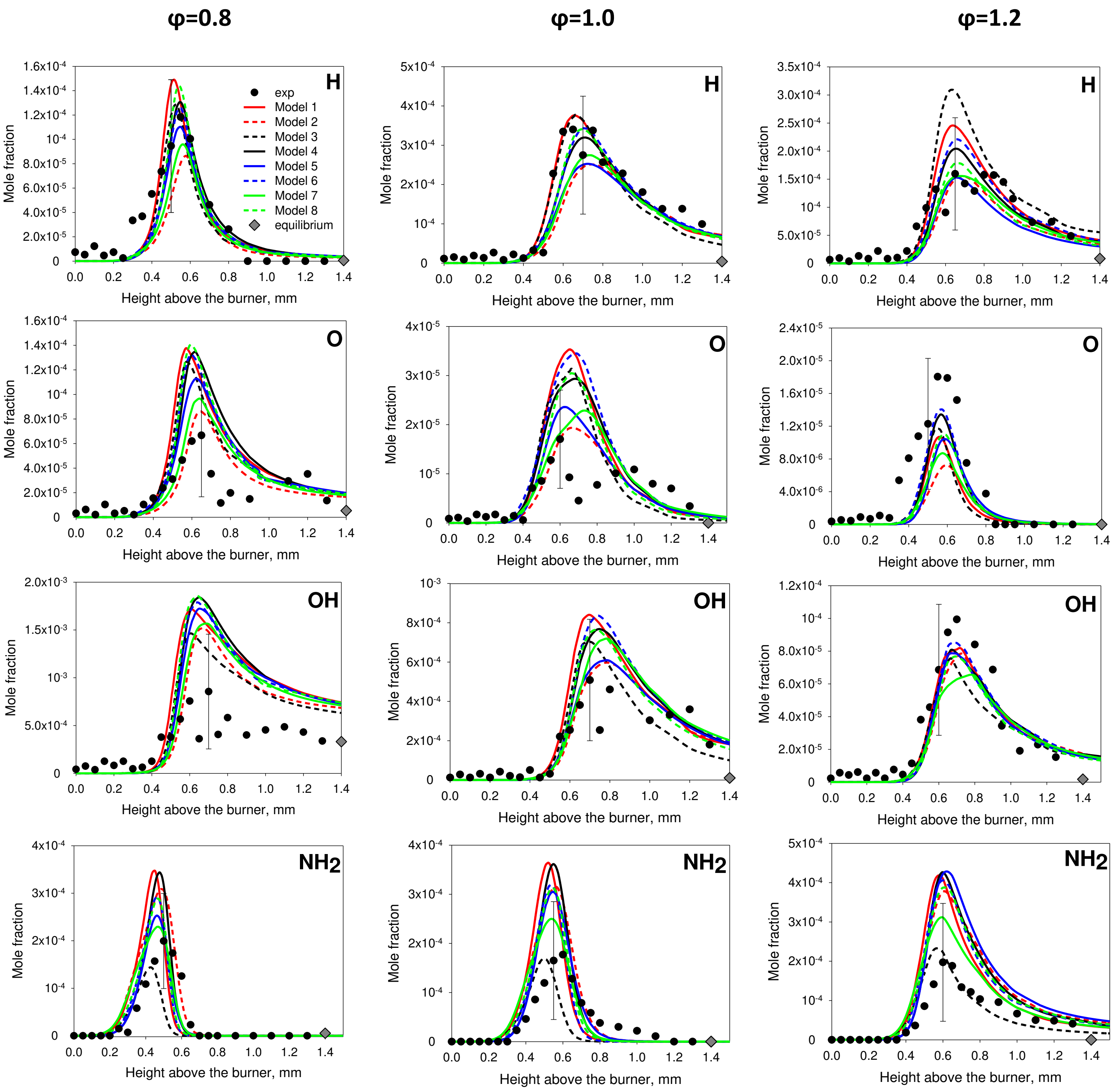
Concentration profiles in rich (φ=1.2) $NH_3/H_2/O_2/Ar$ at P=6 atm – original and modified mechanisms





Mole fraction profiles of H, O, OH and NH$_2$ - radicals in lean, stoichiometric and rich NH$_3$/H$_2$/O$_2$/Ar flames at 4 atm.

Mole fraction profiles of H, O, OH and NH$_2$ -radicals in lean, stoichiometric and rich NH$_3$/H$_2$/O$_2$/Ar flames at 6 atm.



Fuel	NH_3	CH_4	C_3H_8	H_2
Boiling point at 0.1 MPa (°C)	- 33.3	- 161.6	- 42.1	- 252.9
Lower heating value (MJ/kg)	18.6	50.2	46.6	120 .4
Flammability limit (eq. ratio)	0.63～1.40	0.50～1.69	0.51～2.51	0.10～7.17
Maximum burning velocity (m/s)	0.09	0.37	0.43	2.91
Ignition temperature (°C)	651	537	432	500
Maximum adiabatic flame temperature (°C)	1750	1970	2020	2120

Reduction of NOx emissions

For NOx reduction the systems of selective catalytic reduction and/or special additives to fuels are used. The principle: the addition of chemicals which decompose to ammonia, with the further NOx reduction in the following reactions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

$$NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

Ammonia production

Ammonia

Haber–Bosch process: $\mathbf{3H_2+N_2 \text{ -> } 2NH_3}$

T= 500 °C, **p=** 350 **atm**, **porous iron with** $\mathbf{Al_2O_3}$ и $\mathbf{K_2O}$

Ammonia production

Worldwide ammonia production-146 m.t./year

***China* - 48 m.t./year**

***Russia*- 12 m.t./year**

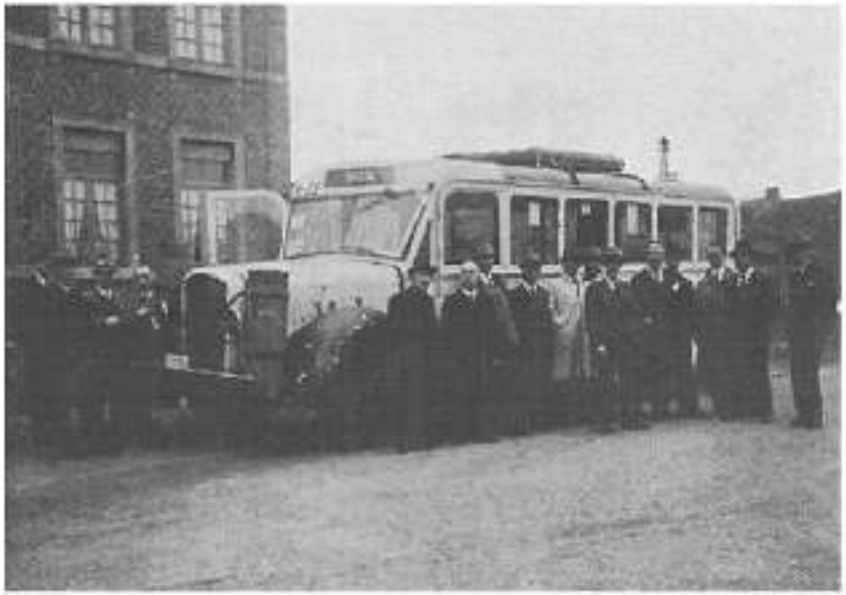
***India* – 11 m.t./year**

***USA* - 9 m.t./year**

A. Valera-Medina, F. Amer-Hatem, A. K. Azad, I. C. Dedoussi, M. de Joannon, R. X. Fernandes, P. Glarborg, H. Hashemi, X. He, S. Mashruk, J. McGowan, C. Mounaim-Rouselle, A. Ortiz-Prado, A. Ortiz-Valera, I. Rossetti, B. Shu, M. Yehia, H. Xiao, and M. Costa. *Review on Ammonia as a Potential Fuel: From Synthesis to Economics* // *Energy Fuels* 2021, 35, 6964−7029.

Flammability limits

Fuel	Lower limit, %	Upper limit, %
Hydrogen	4	75
Methane	4.4	17
Ethane	3	8,5
Ethylene	4	13
Ammonia	15	28



Bus operating on ammonia /coal gas blend, Belgium, 1942 (E. Kroch)

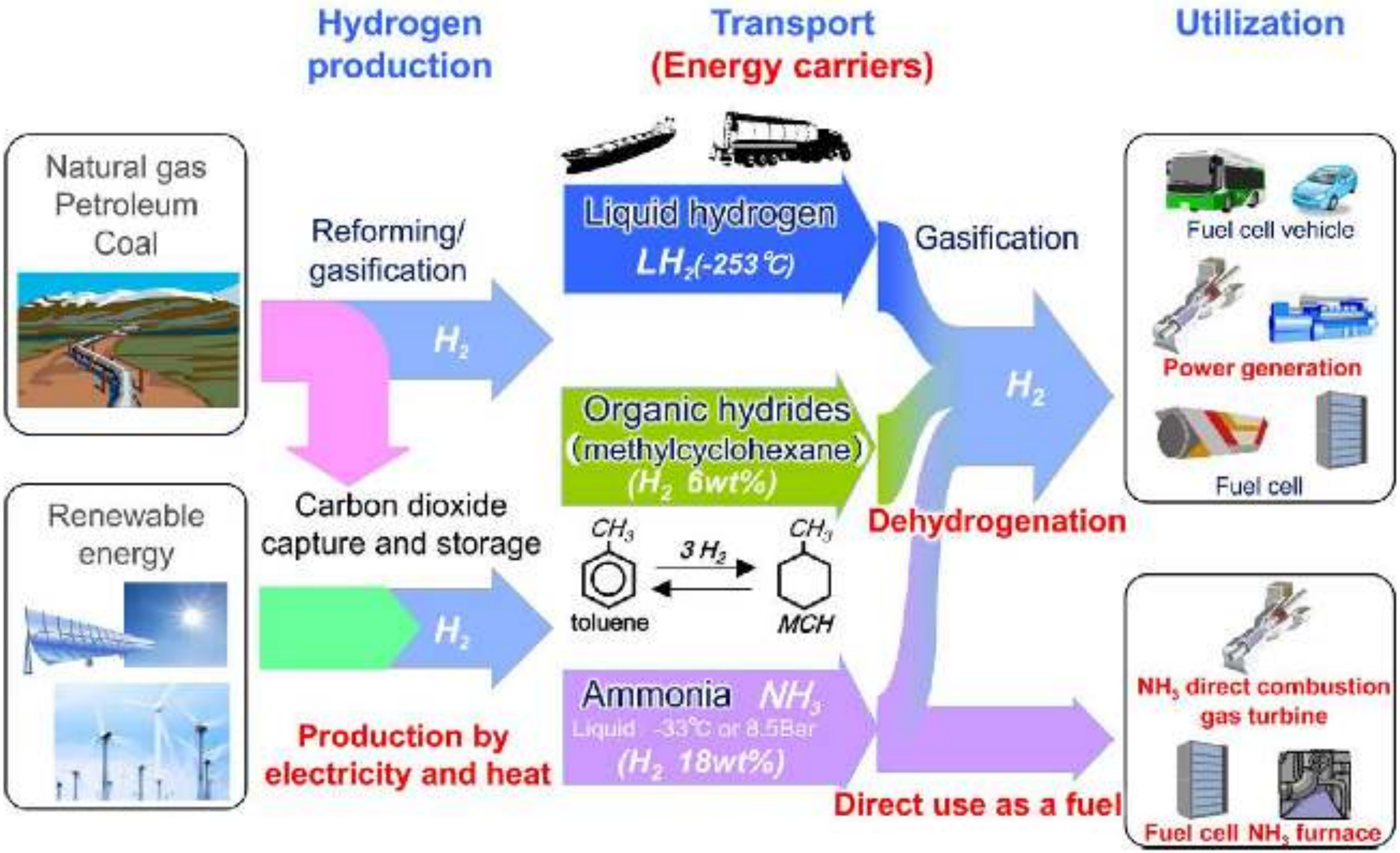
Supersonic X-15 aircraft on NH_3/LOx, USA, 1960http://history.nasa.gov/x15/cover.html

Practical ammonia application for electricity generation

Pilot gas turbine on ammonia-air blend. National Institute of Advanced Industrial Science and Technology, Japan (AIST).

Hideaki Kobayashi, PCI, 2018

Production, transportation and utilization of hydrogen



Hydrogen production

Transport (Energy carriers)

Utilization

Natural gas
Petroleum
Coal

Renewable energy

Reforming/ gasification

H_2

Carbon dioxide capture and storage

H_2

Production by electricity and heat

Liquid hydrogen
LH_2(-253℃)

Organic hydrides
(methylcyclohexane)
(H_2 6wt%)

CH_3 toluene $\underset{}{\overset{3\,H_2}{\rightleftarrows}}$ CH_3 MCH

Ammonia NH_3
Liquid -33℃ or 8.5Bar
(H_2 18wt%)

Gasification

H_2

Dehydrogenation

Direct use as a fuel

Fuel cell vehicle

Power generation

Fuel cell

NH_3 direct combustion gas turbine

Fuel cell **NH_3 furnace**