



Kinetics of the reactions of NO_3 radical with methacrylate esters

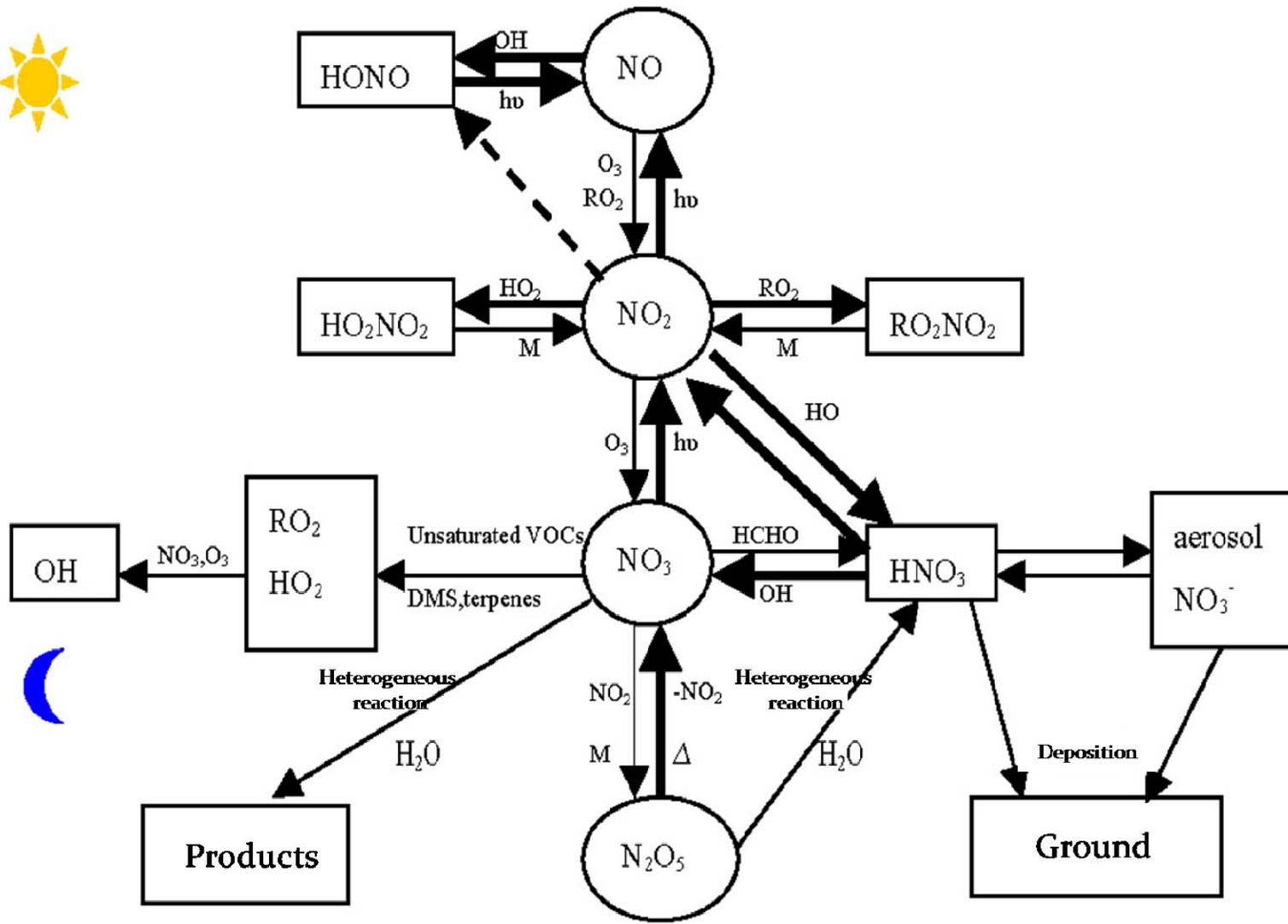
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IDIR, K. ZARZANA, V. DAËLE, A. MELLOUKI

Content

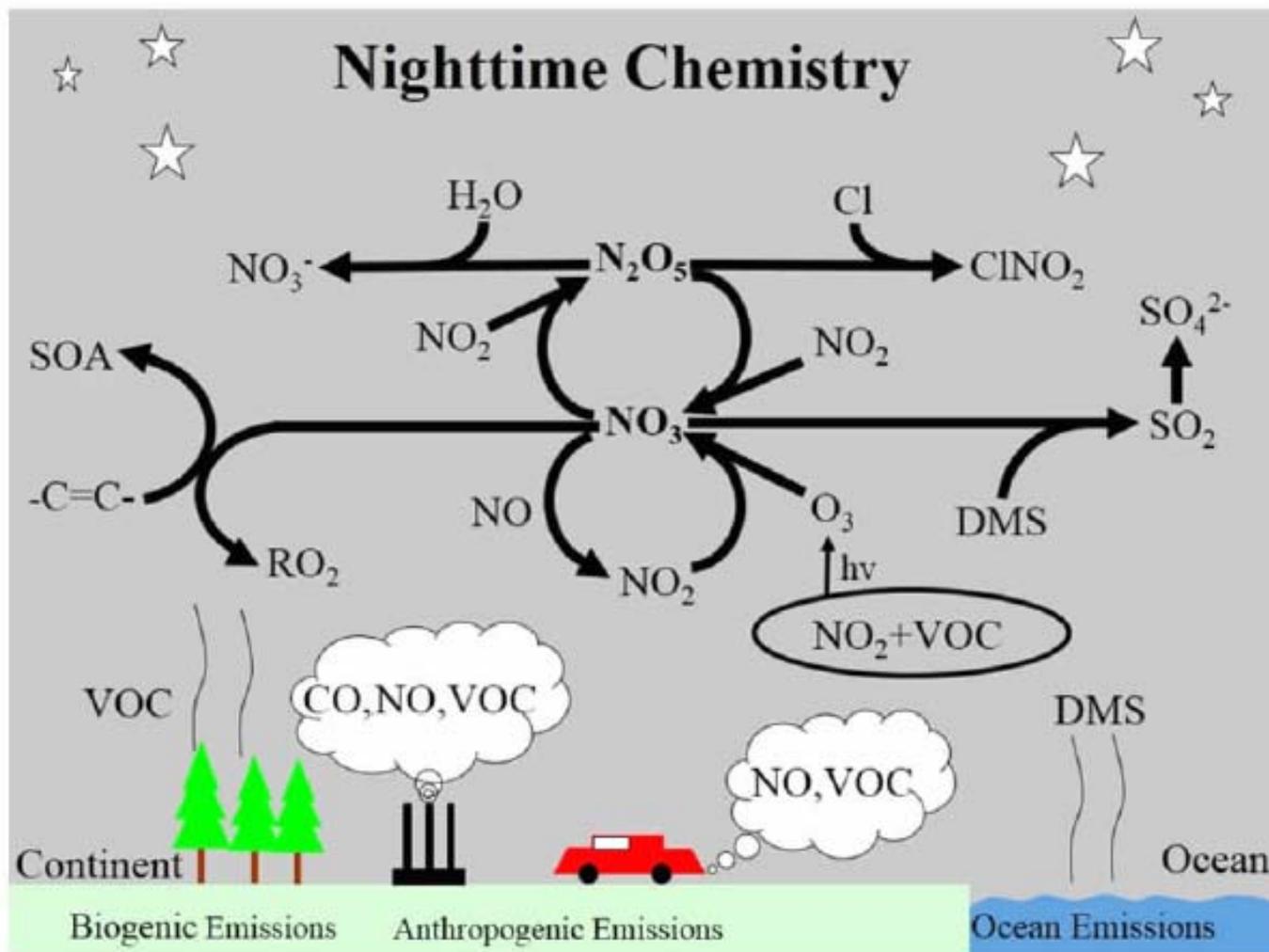
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- ▶ **3 Kinetic study methods and results**
 - 3.1 Relative rate method
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1 Introduction

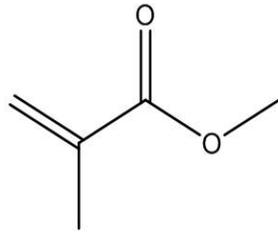


1 Introduction



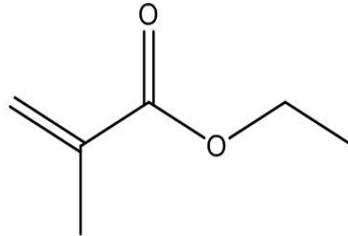
Schematic view of the NO₃ and N₂O₅ atmospheric chemistry in the troposphere

1 Introduction



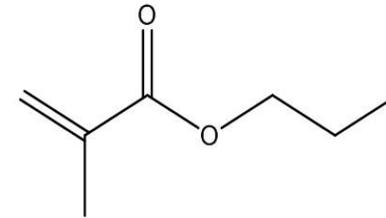
methyl methacrylate

MMA



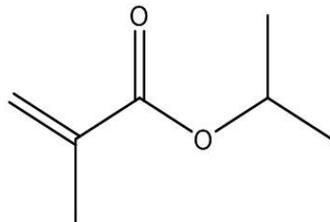
ethyl methacrylate

EMA



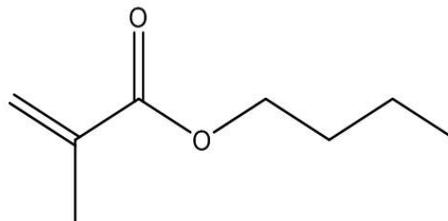
propyl methacrylate

PMA



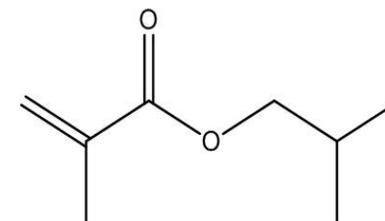
isopropyl methacrylate

IPMA



butyl methacrylate

BMA

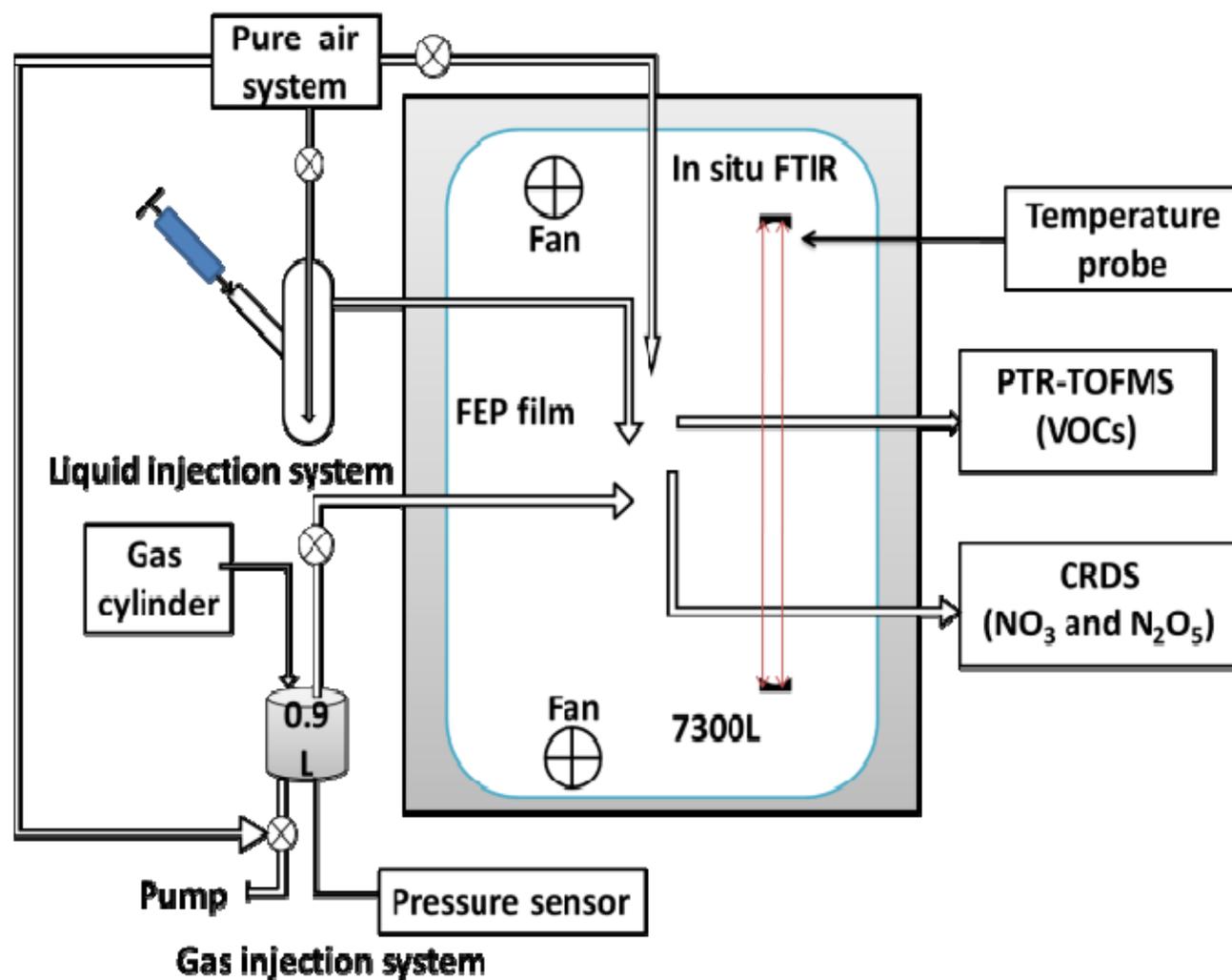


isobutyl methacrylate

IBMA

Methacrylate Esters

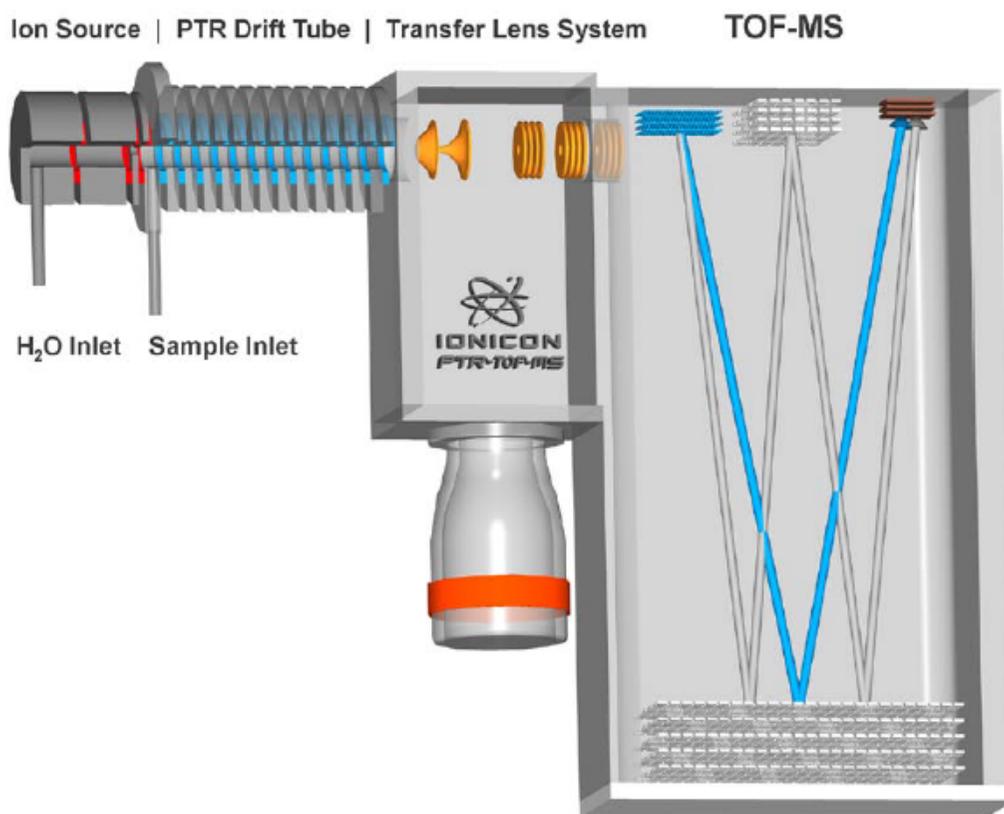
2 Experimental system



Schematic diagram of the 7300 L chamber

PTR-ToF-MS 8000

Proton Transfer Reaction–Mass Spectrometry



Specifications

➤ Detected Items



Gaz

- Mass resolution: $\sim 5000 \text{ m}/\Delta m$
- Response time: 100ms
- Main air pollutants detected

VOC



NO_x, O₃, SO₂



➤ Sensitivity :

Benzene: 20-40 cps/ppbv

Trichlorobenzene: 40-80 cps/ppbv

➤ Limits of Detection

Benzene :10 pptv average over 1 min

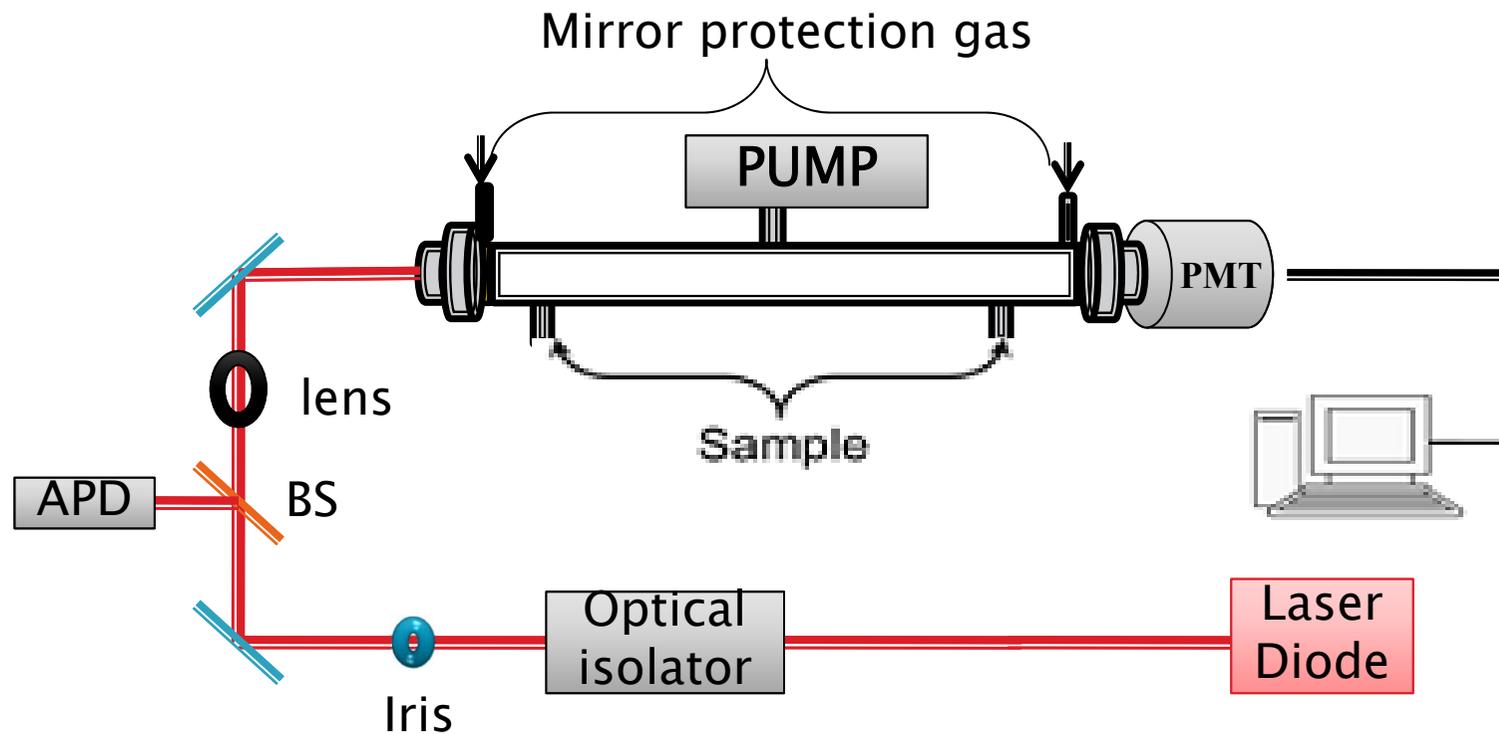
➤ Linearity range :10 pptv - 10 ppmv

➤ Adjustable inlet flow: 50-500sccm

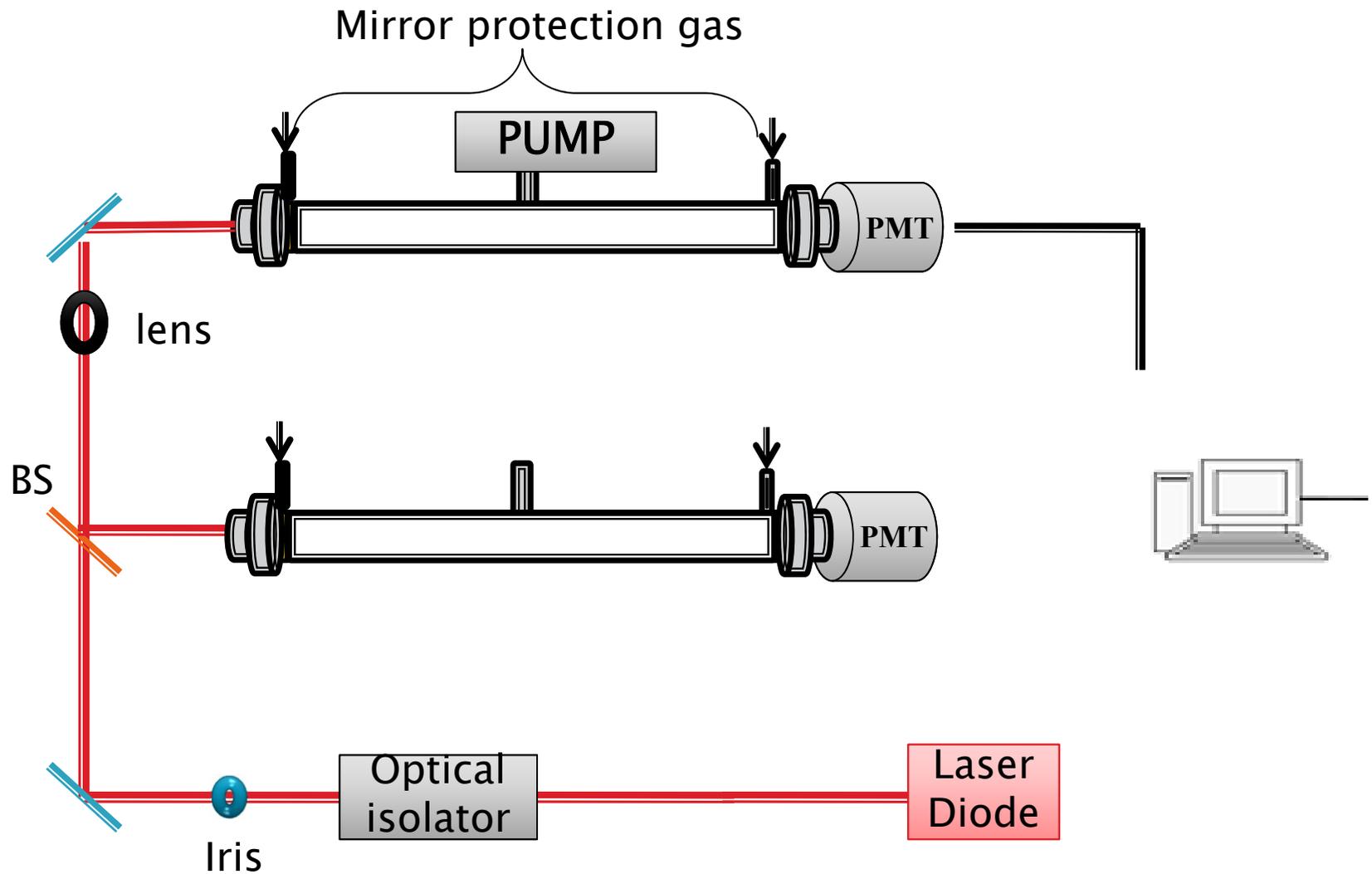
➤ Inlet system heating ($< 150 \text{ }^\circ\text{C}$)

2 Experimental system

Cavity Ring Down Spectrometer (CRDS)



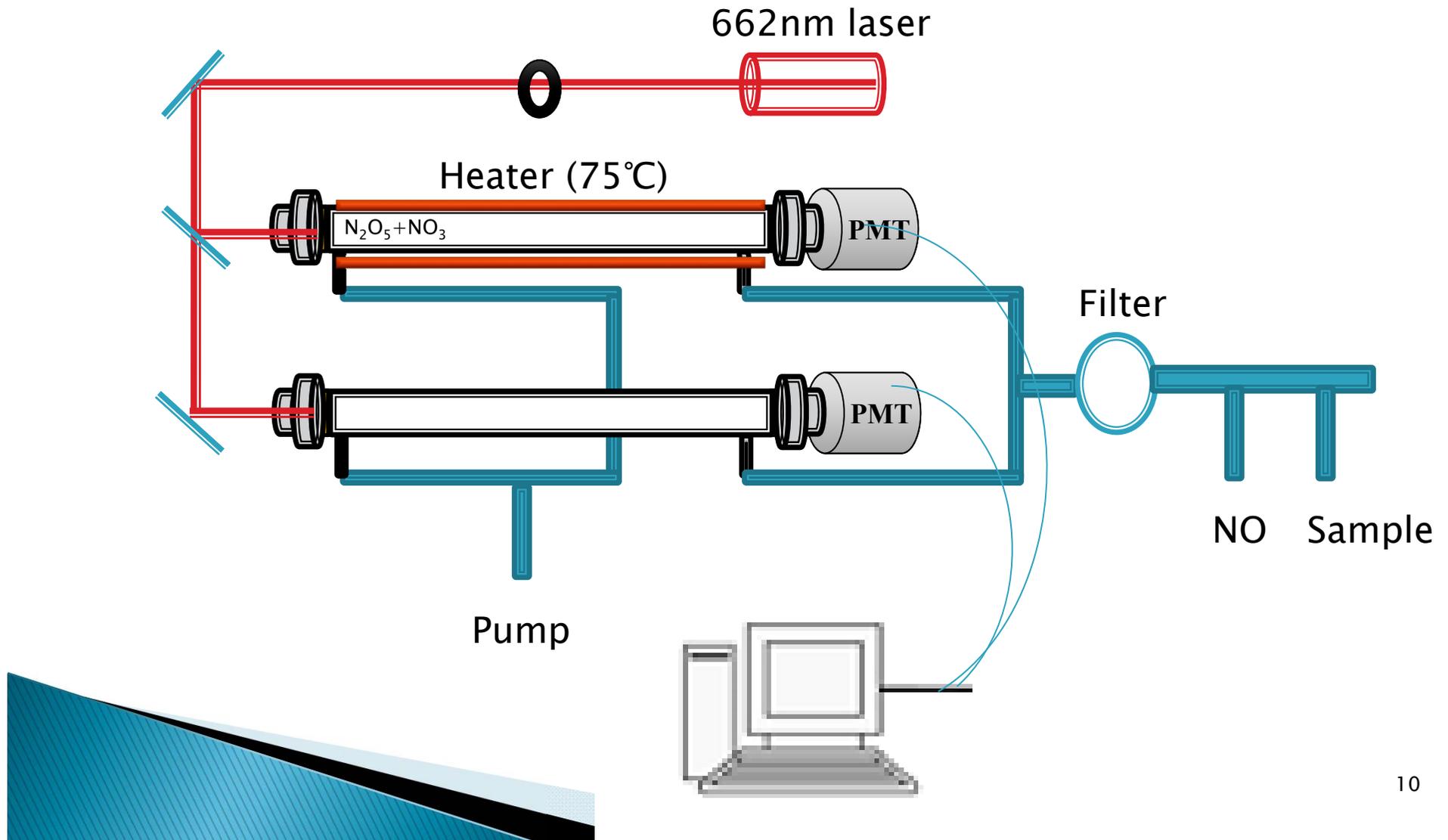
Schematic diagram of the instrument



Schematic diagram of the instrument

2 Experimental system

Cavity Ring Down Spectrometer (CRDS)



3 Kinetic study methods and results

3.1 Relative rate method

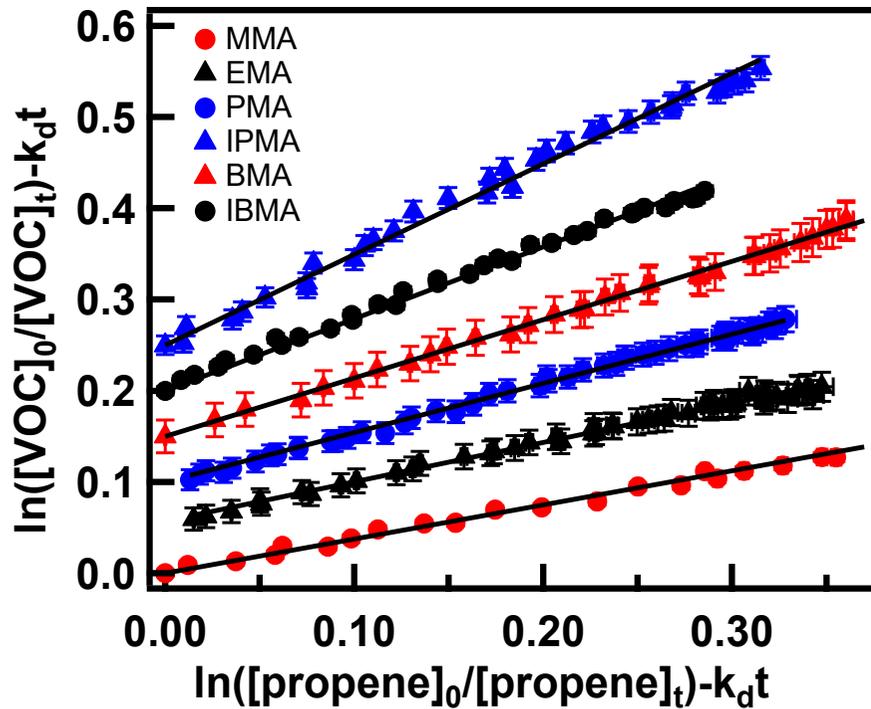


$$-\frac{d[\text{VOC}]}{dt} = k_{\text{voc}}[\text{VOC}][\text{NO}_3] + k_d[\text{VOC}] \quad -\frac{d[\text{Ref}]}{dt} = k_{\text{voc}}[\text{Ref}][\text{NO}_3] + k_d[\text{Ref}]$$

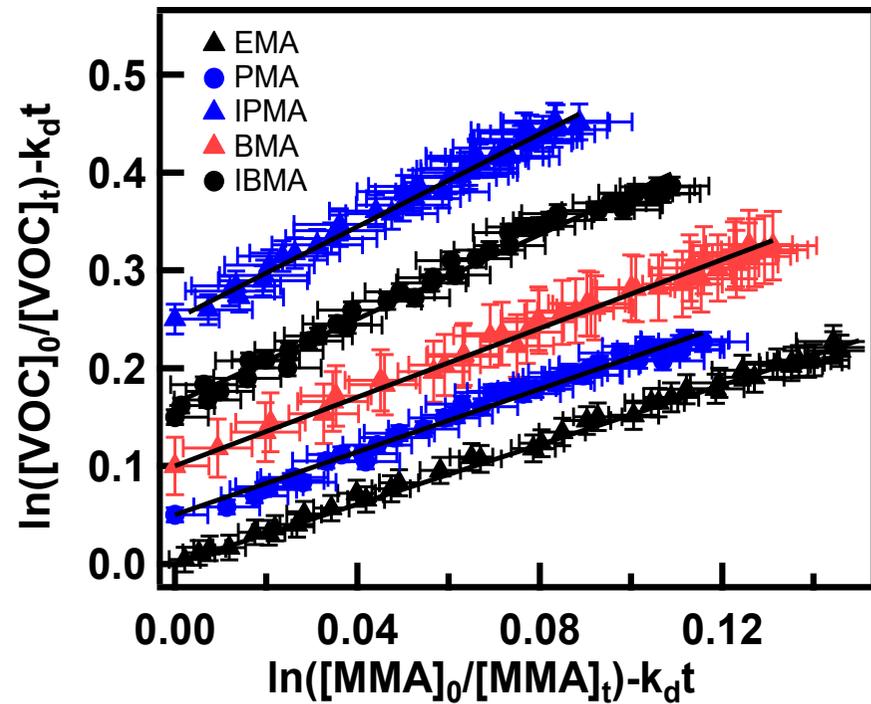
$$\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} = (k_{\text{voc}}[\text{NO}_3] + k_d)t \quad \ln \frac{[\text{Ref}]_0}{[\text{Ref}]_t} = (k_{\text{voc}}[\text{NO}_3] + k_d)t$$

$$\ln \frac{[\text{VOC}]_0}{[\text{VOC}]_t} - k_d \times t = \frac{k_{\text{voc}}}{k_r} (\ln \frac{[\text{Ref}]_0}{[\text{Ref}]_t} - k_d \times t)$$

Plots of the losses of esters relative to references



Propene used as reference



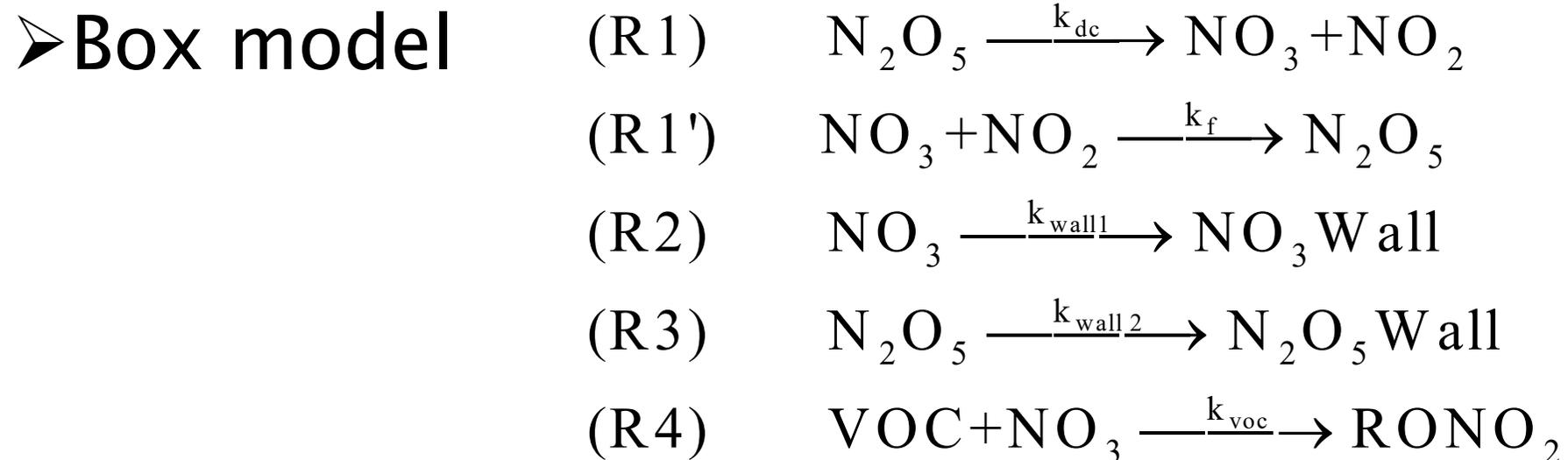
MMA used as reference

Summary of the results from the relative rate study

VOCs	Initial concentration 10^{12} (molecule cm^{-3})	Ref	Number of experiments	$k_{\text{voc}}/k_{\text{r}} \pm$	$k_{\text{voc}} \pm \sigma_{\text{voc}}$ 10^{-15} ($\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$)
Methyl methacrylate (MMA)	1.13 to 3.40	propene	6	0.37 ± 0.04	(3.52 ± 2.07)
		propanal	2	0.58 ± 0.06	(3.77 ± 1.56)
		Weighted average			(3.68 ± 1.24)
Ethyl methacrylate (EMA)	1.28 to 2.56	propene	3	0.53 ± 0.05	(5.04 ± 2.95)
		MMA	2	1.55 ± 0.07	(5.70 ± 1.88)
		Weighted average			(5.51 ± 1.58)
Propyl methacrylate (PMA)	1.10 to 1.66	propene	3	0.56 ± 0.04	(5.32 ± 3.10)
		MMA	3	1.70 ± 0.16	(6.26 ± 2.12)
		Weighted average			(5.96 ± 1.75)
Isopropyl methacrylate (IPMA)	1.10 to 1.65	propene	3	0.91 ± 0.30	(8.65 ± 5.76)
		MMA	3	2.71 ± 0.61	(9.97 ± 3.95)
		Weighted average			(9.55 ± 3.26)
Butyl methacrylate (BMA)	1.01 to 2.53	propene	3	0.70 ± 0.08	(6.65 ± 3.87)
		MMA	3	1.95 ± 0.12	(6.77 ± 2.25)
		Weighted average			(6.74 ± 1.95)
Isobutyl methacrylate (IBMA)	0.99 to 2.48	propene	3	0.75 ± 0.02	(7.13 ± 4.13)
		MMA	3	1.95 ± 0.23	(7.18 ± 2.49)
		Weighted average			(7.16 ± 2.13)

3 Kinetic study methods and results

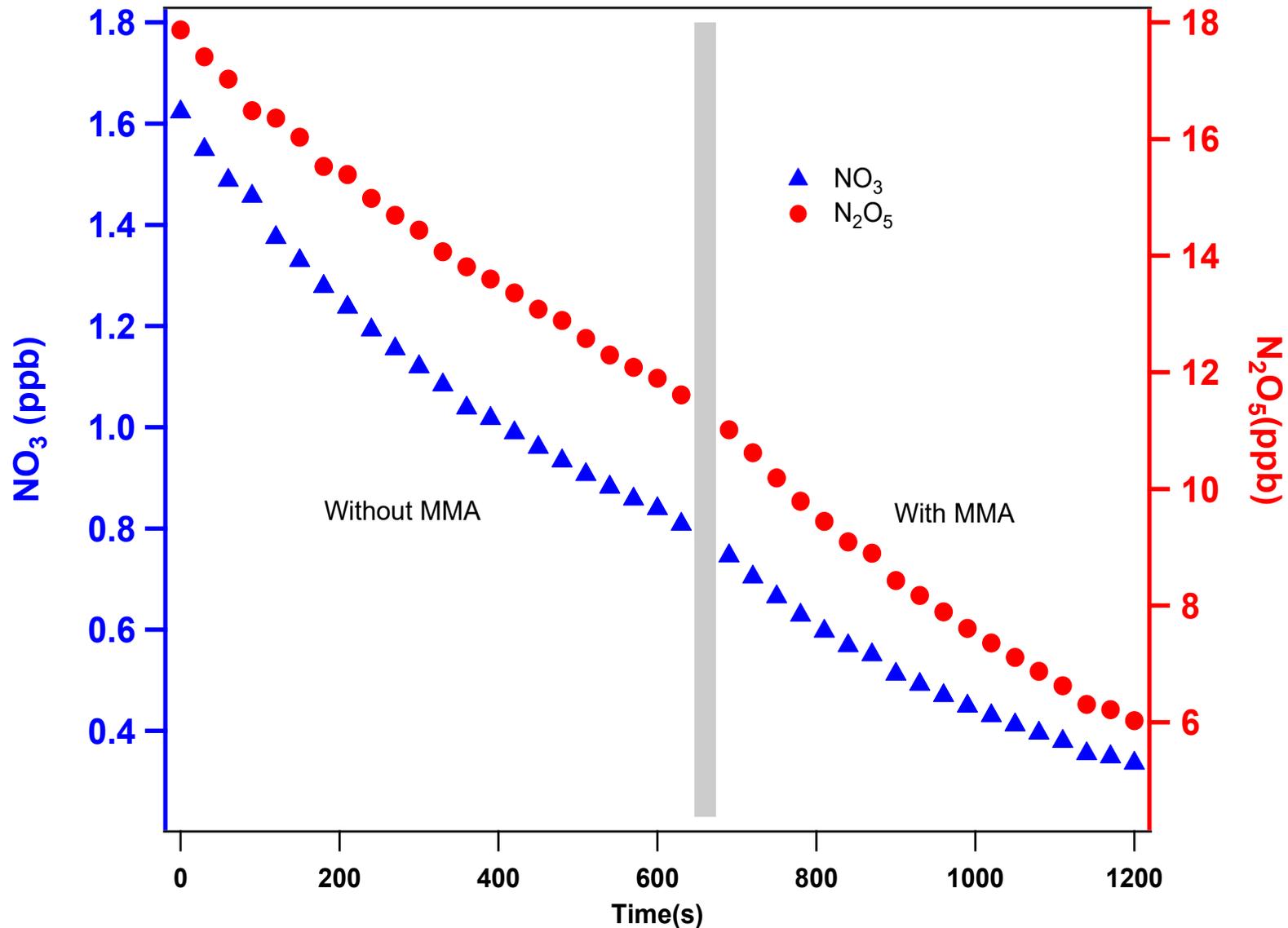
3.2 Rate coefficients via monitoring temporal profiles of $\text{NO}_3/\text{N}_2\text{O}_5$ loss using CRDS



Initial concentration: N_2O_5 , NO_3 , NO_2 , **VOC**

CRDS

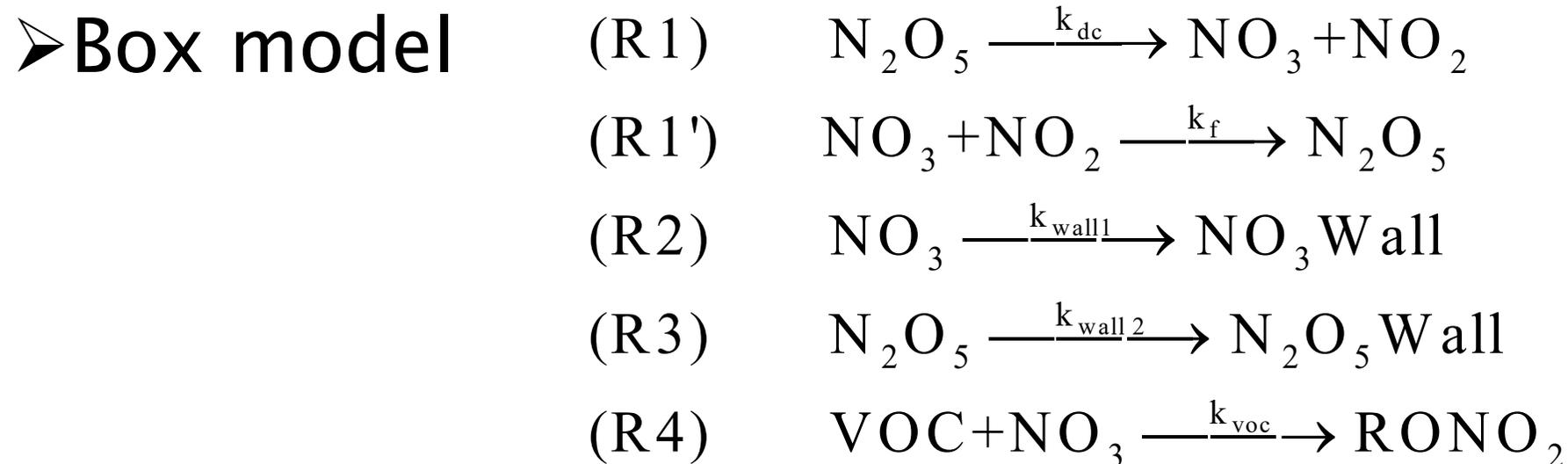
Rate coefficients: k_{dc} , k_{f} , k_{wall1} , k_{wall2} , **k_{voc}**



Profile of NO₃ and N₂O₅ concentration ([NO₃] and [N₂O₅]) loss in the chamber without (up to the gray bar) and with VOCs (MMA) (after the gray bar). The gray bar indicates the time at which VOCs were injected into the chamber and the time it took for complete mixing.

3 Kinetic study methods and results

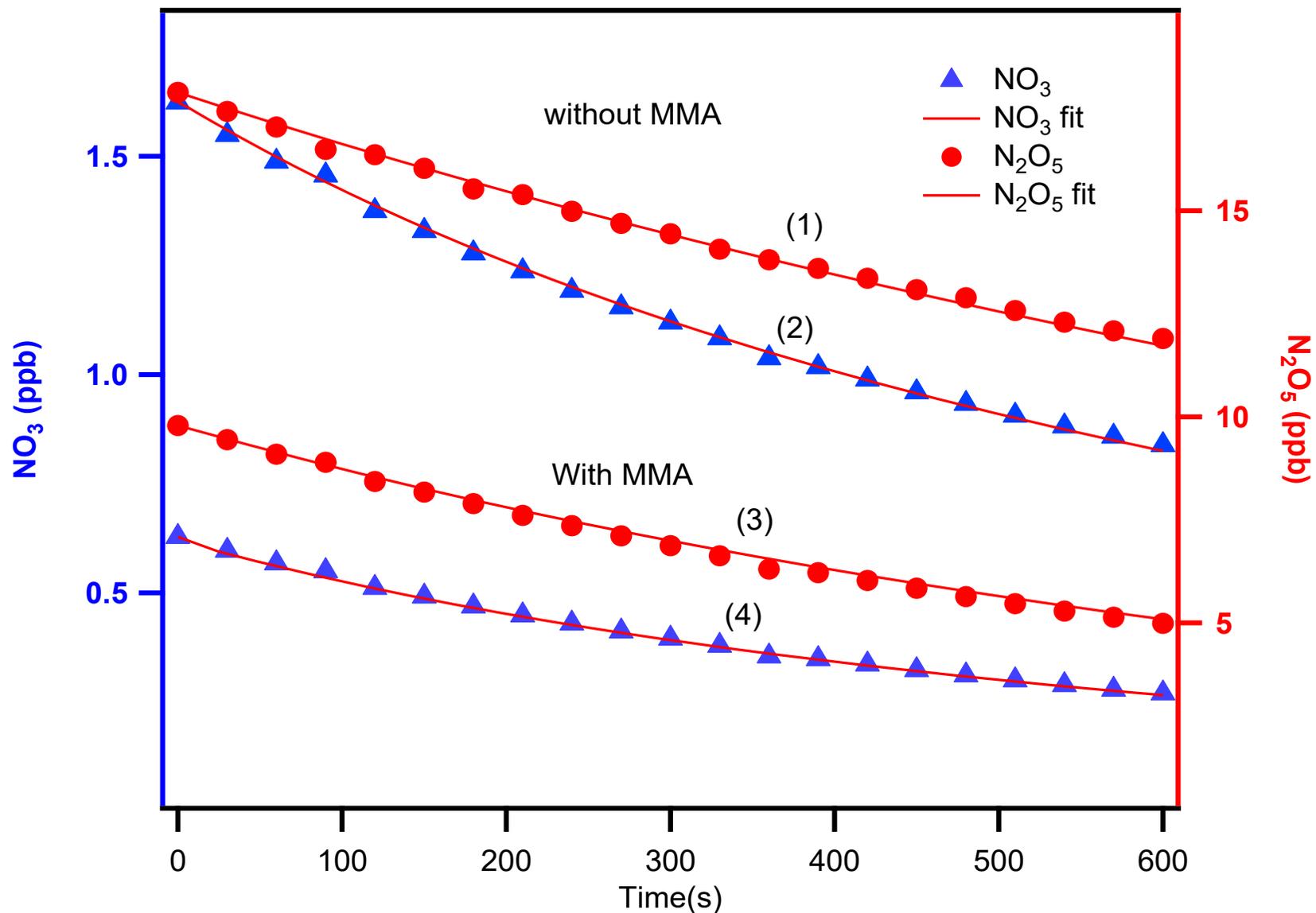
3.2 Rate coefficients via monitoring temporal profiles of $\text{NO}_3/\text{N}_2\text{O}_5$ loss using CRDS



Initial concentration: N_2O_5 , NO_3 , NO_2 , **VOC**

CRDS

Rate coefficients: k_{dc} , k_{f} , k_{wall1} , k_{wall2} , **k_{voc}**



Experimental and simulated results for NO_3 and N_2O_5 profiles from chamber experiments (1) loss of N_2O_5 without MMA (2) loss of NO_3 with MMA (3) loss of N_2O_5 with MMA (4) loss of NO_3 with MMA.

Summary of the experimental conditions and the results from the absolute rate study

Experiment	T(K)	[VOC] ₀ (ppb)	[NO ₃] ₀ (ppb)	[N ₂ O ₅] ₀ (ppb)	k_{VOC} 10 ⁻¹⁵ (molecule ⁻¹ cm ³ s ⁻¹)
propene	296	156.61	0.54	10.16	9.50
	296	70.00	0.45	9.77	9.50
					(9.50 ± 1.90)
MMA	295	121.95	0.68	11.05	3.05
	296	124.30	0.63	9.79	3.00
	298	363.70	0.78	11.46	3.20
					(3.08 ± 0.62)
EMA	298	126.10	0.81	10.85	4.80
	300	130.10	0.59	6.79	5.20
	298	333.30	1.13	16.58	4.85
					(4.95 ± 0.99)
PMA	297	113.47	0.79	11.15	5.20
	300	279.67	1.11	10.13	5.65
	296	113.58	0.83	8.33	5.50
					(5.39 ± 1.08)
IPMA	297	101.60	0.81	10.28	8.50
	296	86.17	0.91	13.01	8.00
	300	209.34	0.84	13.69	8.20
					(8.23 ± 1.65)
BMA	299	264.20	1.00	8.80	5.90
	299	199.19	1.25	11.42	5.80
	300	251.80	1.10	12.92	6.00
					(5.90 ± 1.18)
IBMA	296	142.30	0.77	10.90	6.50
	297	154.50	1.09	13.00	6.80
	297	162.60	0.99	9.44	6.80
					(6.70 ± 1.34)

Rate constants values obtained in two methods for the reactions of NO₃ with methacrylate esters

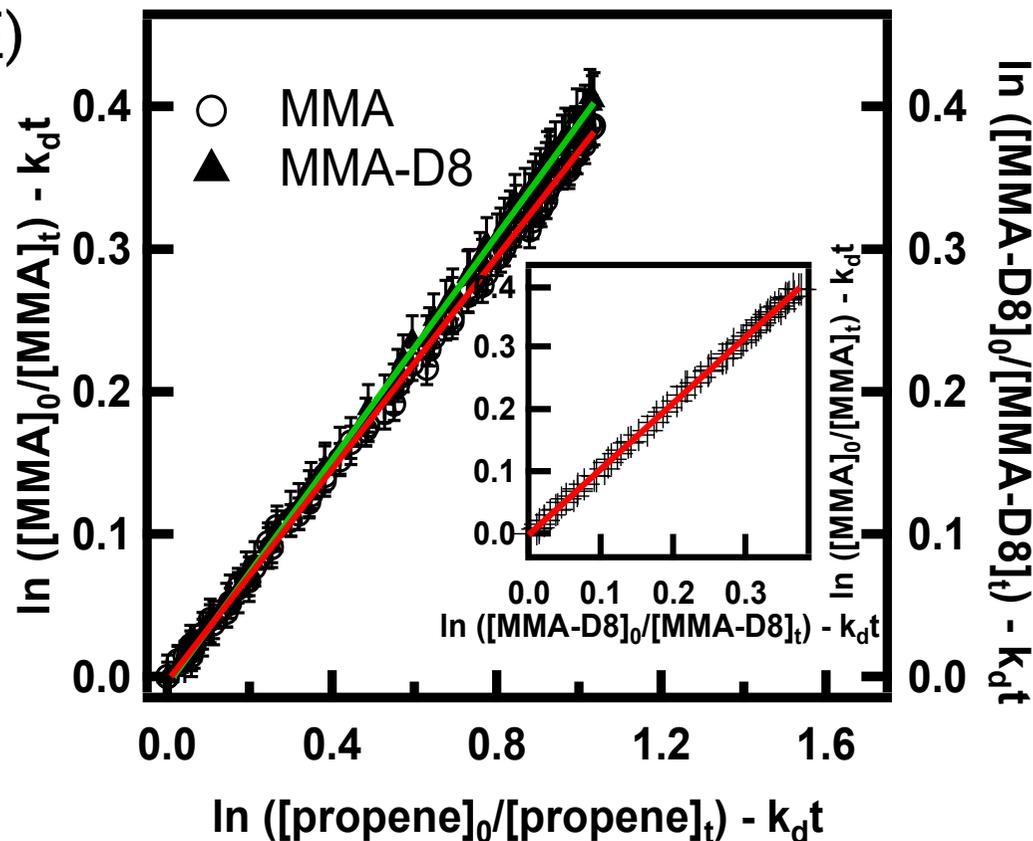
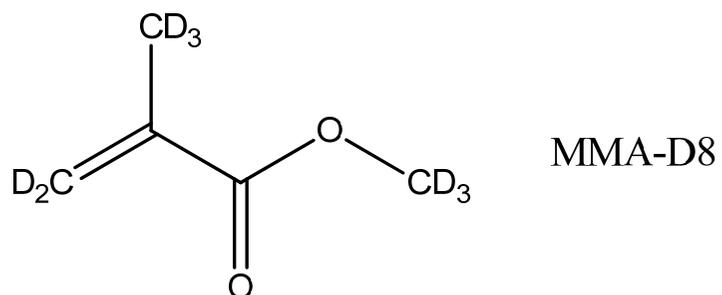
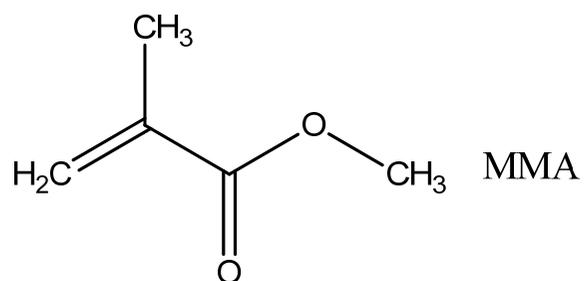
	Rate constants k_{voc} (10^{-15} molecule ⁻¹ cm ³ s ⁻¹)		Ratio ($k_{\text{rm}}/k_{\text{ab}}$)	k_{voc} (10^{-15} molecule ⁻¹ cm ³ s ⁻¹)	
	Relative method (k_{rm})	Absolute method (k_{ab})		Mean average	Weighted average
MMA(k_1)	(3.68±1.24)	(2.92±0.37)	1.26	(3.30±0.65)	(2.98±0.35)
EMA(k_2)	(4.63±0.57)	(4.78±0.93)	0.97	(4.70±0.55)	(4.67±0.49)
PMA(k_3)	(5.08±0.74)	(5.50±1.00)	0.92	(5.29±0.62)	(5.23±0.60)
IPMA(k_4)	(8.14±1.93)	(7.83±1.15)	1.04	(7.99±1.12)	(7.91±1.00)
BMA(k_5)	(5.84±0.76)	(6.00±0.89)	0.97	(5.92±0.59)	(5.91±0.58)
IBMA(k_6)	(5.88±0.94)	(6.60±0.94)	0.89	(6.24±0.66)	(6.24±0.66)

$k_{\text{voc}}(\text{IPMA}) > k_{\text{voc}}(\text{IBMA}) > k_{\text{voc}}(\text{BMA}) > k_{\text{voc}}(\text{PMA}) > k_{\text{voc}}(\text{EMA}) > k_{\text{voc}}(\text{MMA})$

Mechanism

electrophilic addition mechanism

kinetic isotope effect (KIE)



Relative rate plots for the reactions of NO_3 radicals with MMA and MMA-D8 when using propene as a reference. (Inside: relative rate plot for the reaction of NO_3 radicals with MMA-D8 using MMA as reference.)

Atmospheric lifetime

$$\tau = \frac{1}{k_{\text{voc+x}} [\text{X}]}$$

	Rate constants (cm ³ molecule ⁻¹ s ⁻¹)				Lifetime (hours)			
	k _{OH}	k _{NO3}	k _{O3}	k _{Cl}	τ _{OH}	t _{NO3}	t _{O3ⁱ}	t _{Cl}
MMA	(4.2)×10 ⁻¹¹	(2.98)×10 ⁻¹⁵	(7.51)×10 ⁻¹⁸	(2.17)×10 ⁻¹⁰	6.6	186	37	128
EMA	(4.58)×10 ⁻¹¹	(4.67)×10 ⁻¹⁵	(7.68)×10 ⁻¹⁸	(2.71)×10 ⁻¹⁰	6.1	119	36	103
PMA		(5.23)×10 ⁻¹⁵				106	~40	
IPMA		(7.91)×10 ⁻¹⁵				70	~40	
BMA	(7.08)×10 ⁻¹¹	(5.71)×10 ⁻¹⁵		(3.72)×10 ⁻¹⁰	3.3	97	~40	75
IBMA		(6.24)×10 ⁻¹⁵				89	~40	

Thank you for your attention!
Merci!