

Electronic Supplementary Information

Rate coefficient of the reaction $\text{CH}_2\text{OO} + \text{NO}_2$ probed with a quantum-cascade laser near 11 μm

Pei-Ling Luo,^{*†a} Chen-An Chung,^{†b} and Yuan-Pern Lee^{*abc}

^a *Institute of Atomic and Molecular Sciences Academia Sinica, Taipei 10617, Taiwan.*

^b *Department of Applied Chemistry and Institute of Molecular Science National Chiao Tung University, Hsinchu 30010, Taiwan.*

^c *Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan.*

**E-mail: pluo@gate.sinica.edu.tw*

**E-mail: yplee@nctu.edu.tw*

†P.-L. Luo and C.-A. Chung contributed equally to this work.

Part A shows detection sensitivity of CH₂OO and Part B presents kinetic model and experimental details. ESI includes 1 figure and 2 tables.

A. Detection sensitivity of CH₂OO

Figure S1 shows a temporal profile of a line of CH₂OO at 925.176 cm⁻¹. The root-mean-square noise level is $\sim 1.4 \times 10^{-5}$ at the later stage (7.2–7.8 ms) of the decay and the maximal absorbance is $\sim 1.72 \times 10^{-3}$; the ratio of signal to noise (S/N) is hence ~ 123 . According to the method and kinetic model discussed in Sec. B, $[\text{CH}_2\text{OO}]_0 = 4.82 \times 10^{12}$ molecule cm⁻³. The minimal detectable $[\text{CH}_2\text{OO}]_0$ is hence $\sim 3.9 \times 10^{10}$ molecule cm⁻³. When we monitored the most intense line at 896.876 cm⁻¹, its intensity is ~ 3 times that of the line at 925.176 cm⁻¹ and the noise level is similar; a minimal detectable $[\text{CH}_2\text{OO}]_0$ is hence $\sim 1.3 \times 10^{10}$ molecule cm⁻³.

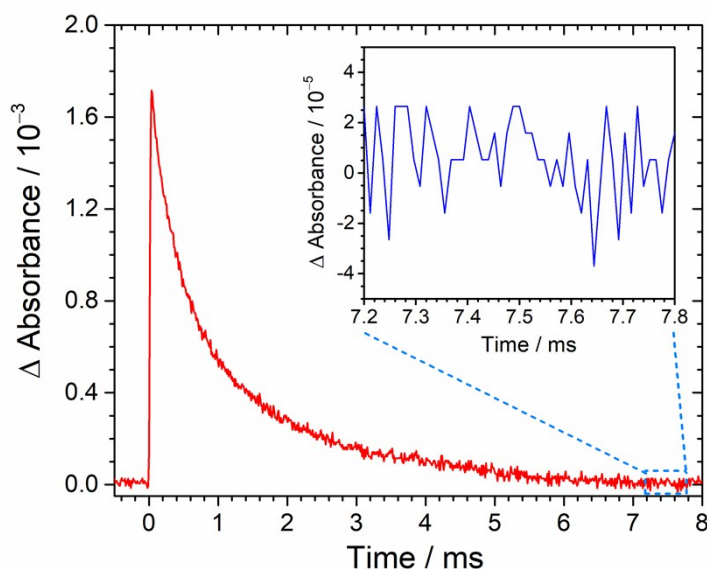


Figure S1. Temporal profile of a line of CH₂OO at 925.176 cm⁻¹. The estimated initial concentration is 4.82×10^{12} molecule cm⁻³ and the S/N ratio of this trace is ~ 123 , yielding a minimum detectable $[\text{CH}_2\text{OO}]_0 \sim 3.9 \times 10^{10}$ molecule cm⁻³.

B. Kinetic model and experimental details

The initial concentration of CH₂I, $[\text{CH}_2\text{I}]_0$, was estimated from photolysis of CH₂I₂ with the initial concentration $[\text{CH}_2\text{I}_2]_0$ according to the equation

$$[\text{CH}_2\text{I}]_0 = [\text{CH}_2\text{I}_2]_0 \times (F/h\nu) \times \sigma_{\text{CH}_2\text{I}_2} \times y \quad (1)$$

in which F is fluence of the photolysis laser light, $h\nu$ is the photon energy, $\sigma_{\text{CH}_2\text{I}_2} = 1.59 \times 10^{-18}$ cm² molecule⁻¹ is the absorption cross section of CH₂I₂ at 248 nm,¹ and quantum yield y of CH₂I is assumed to be 1. To determine the rate coefficients of CH₂OO + NO₂, we employed a kinetic model slightly modified from that of our previous report,² as listed in Table S1, to fit the observed temporal profiles.

Possible reaction paths including the formation, decomposition, and self-reaction of CH₂OO, and the reactions CH₂OO + NO₂, O(³P) + CH₂I₂, CH₂I + NO₂, O(³P) + CH₂I, and O(³P) + CH₂OO were included in this kinetic model. We fixed the rate coefficients at values listed in Table S1, input [CH₂I]₀, [O₂]₀, and [NO₂]₀, and varied the first-order rate coefficient k^I ($= k_{10} \times [\text{NO}_2]_0$ in Table S1) of the title reaction to fit the temporal profiles of the probed absorption line of CH₂OO. The experimental conditions and the model-fitted first-order rate coefficients k^I in all 24 measurements (in four sets) are summarized in Table S2.

Table S1. Kinetic model and rate coefficients employed in the fitting for CH₂OO + NO₂

Reaction	Rate coefficient ^a	Ref.
k_{1a}^b CH ₂ I + O ₂ → CH ₂ OO + I	$\{1 - 0.47/(1+3.2\times 10^{-18} [M])\} \times 1.6\times 10^{-12} / (1+1.1\times 10^{-19} [M])$	2
k_{1b}^b CH ₂ I + O ₂ → CH ₂ IOO	$1.6\times 10^{-12} - 1.6\times 10^{-12} / (1+1.1\times 10^{-19} [M])$	2
k_{1c}^b CH ₂ I + O ₂ → CH ₂ O + IO	4.0×10^{-13}	3
k_{1d}^b CH ₂ I + O ₂ → other products	$1.6\times 10^{-12} - k_{1a} - k_{1b} - k_{1c}$	2
k_{2a} CH ₂ OO + I → CH ₂ I + O ₂	$55 \times 1.6\times 10^{-12} / (1+1.1\times 10^{-19} [M])$	2
k_{2b} CH ₂ OO + I → CH ₂ IOO	$55 \times \{1.6\times 10^{-12} - 1.6\times 10^{-12} / (1+1.1\times 10^{-19} [M])\}$	2
k_{2c} CH ₂ OO + I → CH ₂ O + IO	9.0×10^{-12}	2
k_3 CH ₂ OO + CH ₂ I → C ₂ H ₄ I + O ₂	6.3×10^{-11}	4
k_{self} CH ₂ OO + CH ₂ OO → 2CH ₂ O + O ₂	9.2×10^{-12}	5
k_5 IO + IO → I ₂ + O ₂	9.9×10^{-11}	6
k_6 CH ₂ IOO + I → CH ₂ IO + IO	3.5×10^{-11}	7
k_7 CH ₂ IOO + CH ₂ IOO → 2CH ₂ IO + O ₂	9.0×10^{-11}	7
k_8 CH ₂ IO → CH ₂ O + I	10^6 s^{-1}	7
k_9 CH ₂ I + NO ₂ → products	2.2×10^{-11}	8
k_{10} CH ₂ OO + NO ₂ → products	$k^l = k_{10} \times [\text{NO}_2]_0$, fitted	
k_{11} O(³ P) + CH ₂ I ₂ → CH ₂ I + IO	7.4×10^{-11}	9
k_{12} O(³ P) + CH ₂ I → products	1.0×10^{-10}	^c
k_{13} O(³ P) + CH ₂ OO → products	1.0×10^{-10}	^c

^a Rate coefficient in cm³ molecule⁻¹ s⁻¹, unless specified, [M] in molecule cm⁻³. ^b $k_{1a}^b + k_{1b} + k_{1c} + k_{1d} = 1.6\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^c estimated values.

Table S2. Summary of experimental conditions and fitted rate coefficients

Set	Expt.	Probe line /cm ⁻¹	fluence /mJ cm ⁻²	[CH ₂ I ₂] ₀ /mTorr	[O(³ P)] ₀ /10 ¹¹ ^a	[CH ₂ I] ₀ /10 ¹² ^a	[CH ₂ OO] ₀ /10 ¹² ^a	[NO ₂] ₀ /10 ¹⁴ ^a	[O ₂] /Torr	reaction /% ^b	<i>k</i> ^t /s ⁻¹
1	1	919.14	15	5.6	0.6	5.4	4.3	3.5	9.6	35	619
	2	919.14	15	5.6	0.9	5.4	4.3	4.7	9.6	42	818
	3	919.14	15	5.6	2.2	5.4	4.3	11.9	9.6	62	1403
	4	919.14	15	5.6	3.7	5.4	4.3	20.3	9.6	72	1986
	5	919.14	15	5.6	6.0	5.4	4.3	32.7	9.6	78	3357
	6	919.14	15	5.6	8.2	5.4	4.3	45.0	9.6	81	4784
	7	919.14	15	5.6	10.1	5.4	4.3	55.3	9.6	82	5851
	8	919.14	15	5.6	10.8	5.4	4.3	59.2	9.6	83	6269
	9	919.14	15	5.6	11.7	5.4	4.3	64.3	9.6	84	6783
2	10	919.14	15	3.6	0.4	3.5	2.8	2.1	5.8	35	289
	11	919.14	15	3.6	0.7	3.5	2.8	3.7	5.8	47	570
	12	919.14	15	3.6	0.9	3.5	2.8	4.9	5.8	54	611
	13	919.14	15	3.6	2.0	3.5	2.8	10.8	5.8	71	1134
	14	919.14	15	3.6	2.9	3.5	2.8	15.9	5.8	77	1658
	15	919.14	15	3.6	4.0	3.5	2.8	21.8	5.8	81	2398
	16	919.14	15	3.6	5.2	3.5	2.8	28.4	5.8	83	2853
	17	919.14	15	3.6	6.3	3.5	2.8	34.7	5.8	85	3950
	18	919.14	15	3.6	7.0	3.5	2.8	38.5	5.8	85	4120
3	19	918.73	7	25.0	0.4	12.1	9.6	4.4	6.3	24	529
	20	918.73	7	25.0	1.7	12.1	9.6	18.8	6.3	51	1685
	21	918.73	7	25.0	3.5	12.1	9.6	39.8	6.3	59	4137
4	22	918.73	7	26.9	0.5	12.1	9.6	5.6	9.5	27	740
	23	918.73	7	26.9	2.1	12.1	9.6	23.4	9.5	55	2385
	24	918.73	7	26.9	4.5	12.1	9.6	50.6	9.5	64	4969

^a in unit of molecule cm⁻³.^b percentage CH₂OO consumed by the reaction with NO₂.

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