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Infrared Absorption Spectrum of Chloromethyl Hydroperoxide [CH_2ClOOH] Produced in the Reaction of the Criegee Intermediate CH_2OO with HCl

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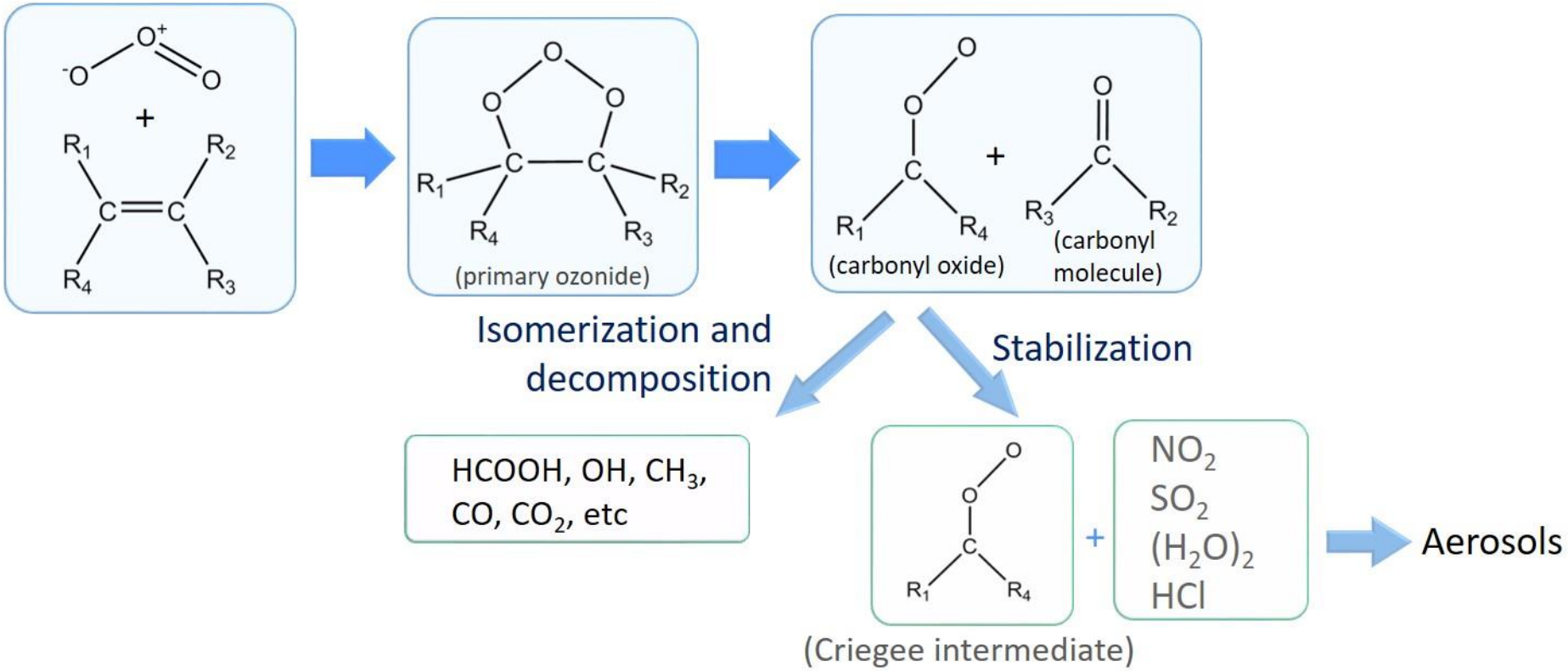
Jun. 22, 2018

Importance of Criegee intermediates



- **Criegee mechanism:**
  production of OH radicals in the atmosphere
- **Reaction with atmospheric species:**
  formation of organic acids and aerosols in the atmosphere

R. Criegee, *Rec. Chem. Prog*. **18**, 111 (1957)

Important reactions of CH_2OO (298 K)

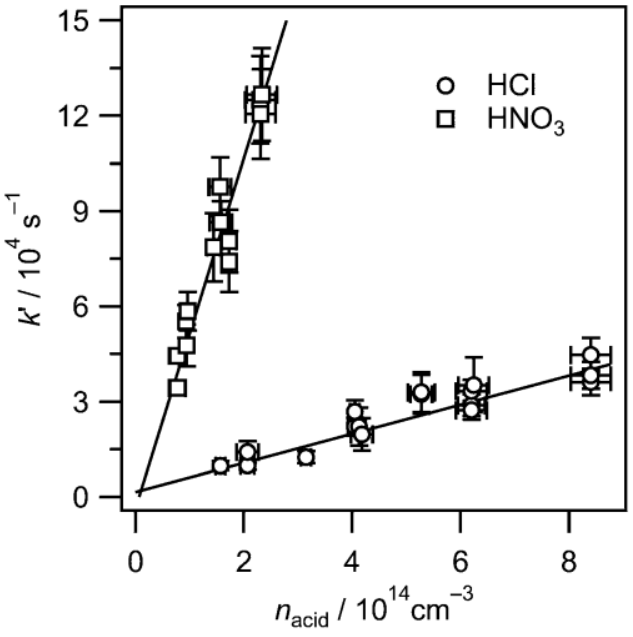
Reactions	Rate coefficients	Ref.
$CH_2OO + CH_2OO \rightarrow 2\ CH_2O + O_2$	$k = (8 \pm 4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}	1-3
$CH_2OO + SO_2 \rightarrow H_2CO + SO_3$	$k = (3.8 - 4.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}	3-7
$CH_2OO + (H_2O)_2 \rightarrow$ product	$k = (4.0 - 6.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}	8,9
$CH_2OO + HCOOH \rightarrow$ product	$k = (1.1 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}	10
$CH_2OO + HNO_3 \rightarrow$ product	$k = (5.4 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}	11

Reference

1. Ting et al. *JCP.* **141**, 104308 (2014)
2. Buras et al., *JPCL.* **5(13)**, 2224 (2014).
3. Chhantyal-pun et al., *PCCP.* **17**, 3617 (2015).
4. Welz et al., *Science* **335**, 204 (2012).
5. Stone et al, *PCCP.* **16**, 1139 (2014).
6. Liu et al., *JPC. A* **118**, 741 (2014).
7. Sheps et al., *JPCL.* **4**, 4201 (2013).
8. Chao et al., *Science* **347**, 751 (2015).
9. Lewis et al., *PCCP.* **17**, 4859 (2015).
10. Welz et al., *ACIE.* **53**,4547 (2014)
11. Elizabeth et al. ,*ACIE*., **55**, 1 (2016)

Importance of CH_2OO + HCl reaction

- UV absorption spectroscopy



CH_2OO + HCl

$k = 4.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (at 27-35 Torr)

Elizabeth et al., Angew. Chem. Int. Ed. , 55, 1(2016)

[HCl] = 3.5×10^{10} molecule cm^{-3}

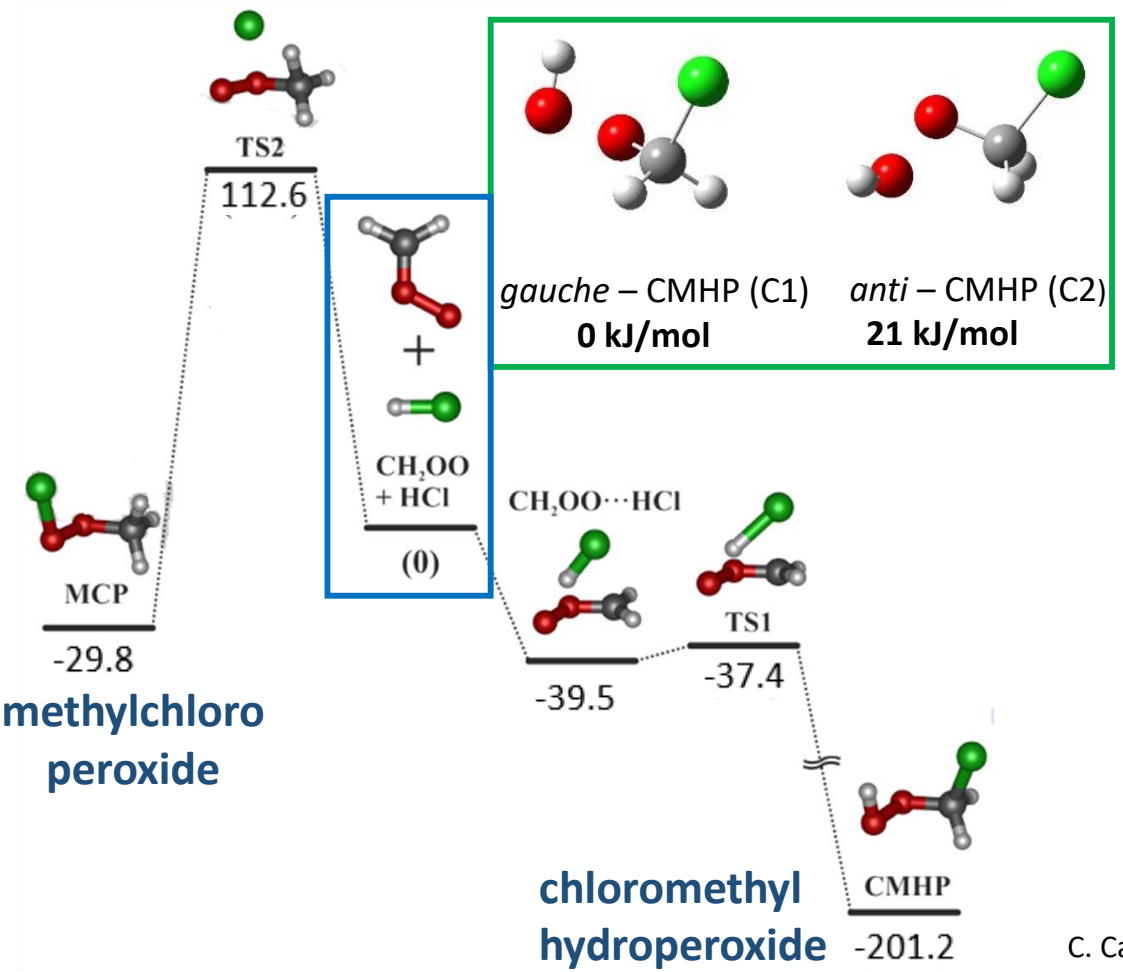
$k_{eff} = k$ [HCl] = 1.6 s^{-1}

coreactant	k_{TS} (cm^3 $molecule^{-1}$ s^{-1})	molecules cm^{-3}	k_{eff} (s^{-1})
H_2O	10^{-16}	10^{17}	10
$(H_2O)_2$	10^{-11}	10^{14}	10^3
H_2S	10^{-15}	10^{11}	10^{-4}
SO_2	10^{-11}	10^{10}	10^{-1}
NO_2	10^{-12}	10^9	10^{-3}
NH_3	10^{-13}	10^{11}	10^{-2}
HO_2	10^{-10}	10^8	10^{-2}
OH	10^{-12}	10^5	10^{-7}
RO_2	10^{-12}	10^8	10^{-4}
H_2SO_4	10^{-12}	10^6	10^{-6}
HNO_3	10^{-10}	10^{11}	10
RCOOH	10^{-10}	10^{10}	1
CO	10^{-24}	10^{12}	10^{-12}
NO	10^{-18}	10^8	10^{-10}
CO_2	10^{-19}	10^{16}	10^{-3}

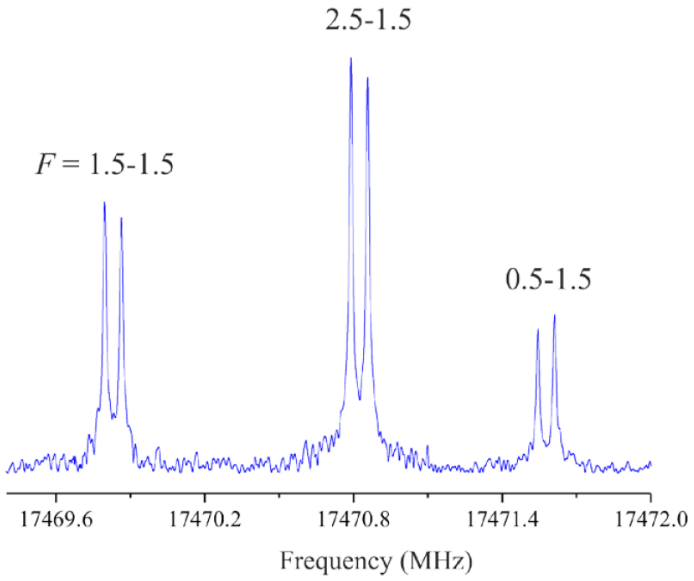
Crisp et al., J. Geophys. Res. Atmos.,119, 6897(2014)

Kumar et al., J. Phys. Chem. Lett., 8, 4206−4213 (2017)

Previous investigations on CH_2OO + HCl



- FTMW spectroscopy



$CH_2I + O_2 \longrightarrow CH_2OO$

$CH_2OO + HCl \longrightarrow CH_2ClOOH$ (C1)

C. Cabezas and Y. Endo, ChemPhysChem. 2017, 18, 1860-1863

step-scan time-resolved FTIR absorption spectrometer

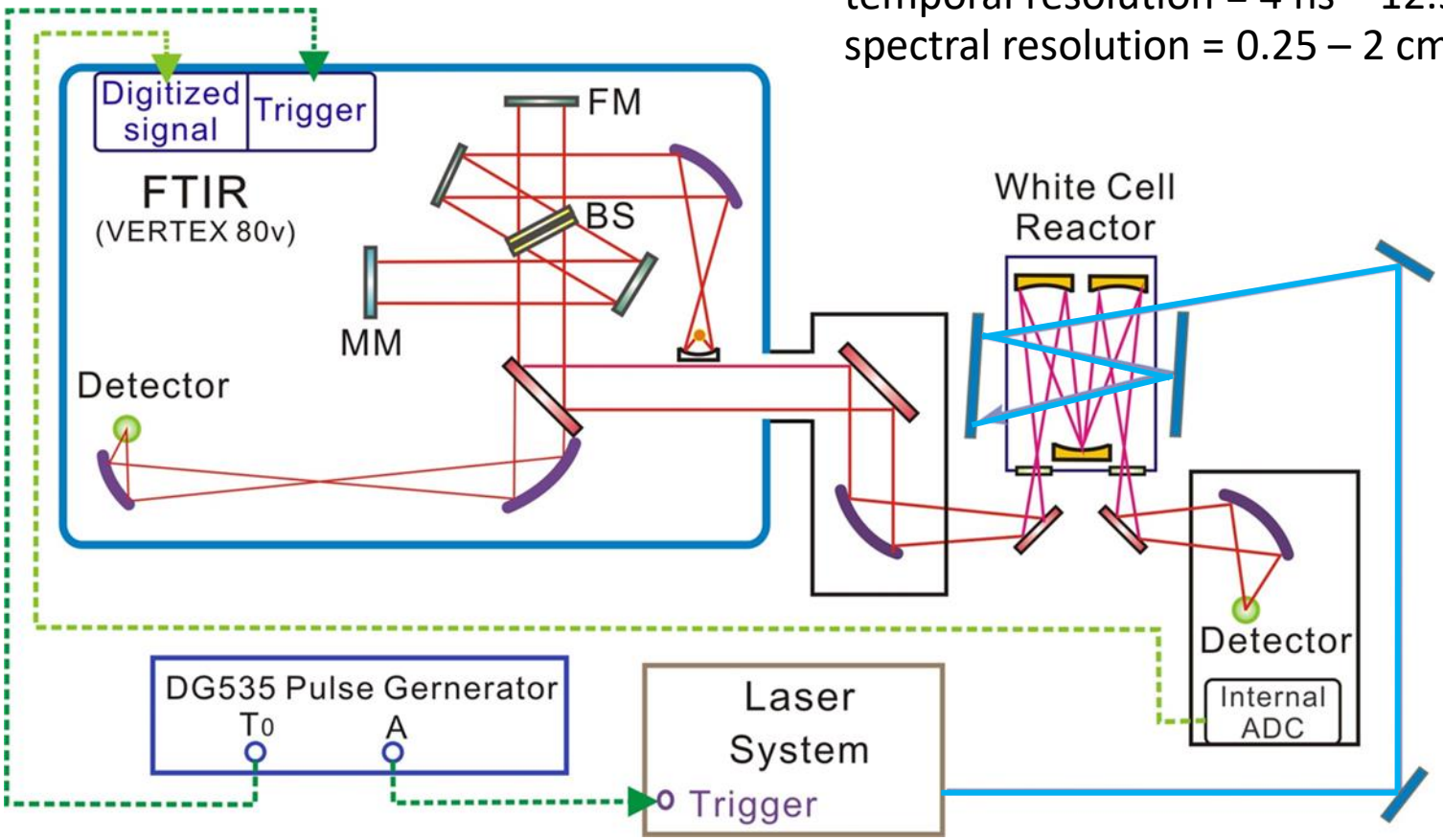
Step-scan FTIR absorption spectrometer

$CH_2I_2 \xrightarrow{308nm} CH_2I + I$

$CH_2I + O_2 \longrightarrow CH_2OO$

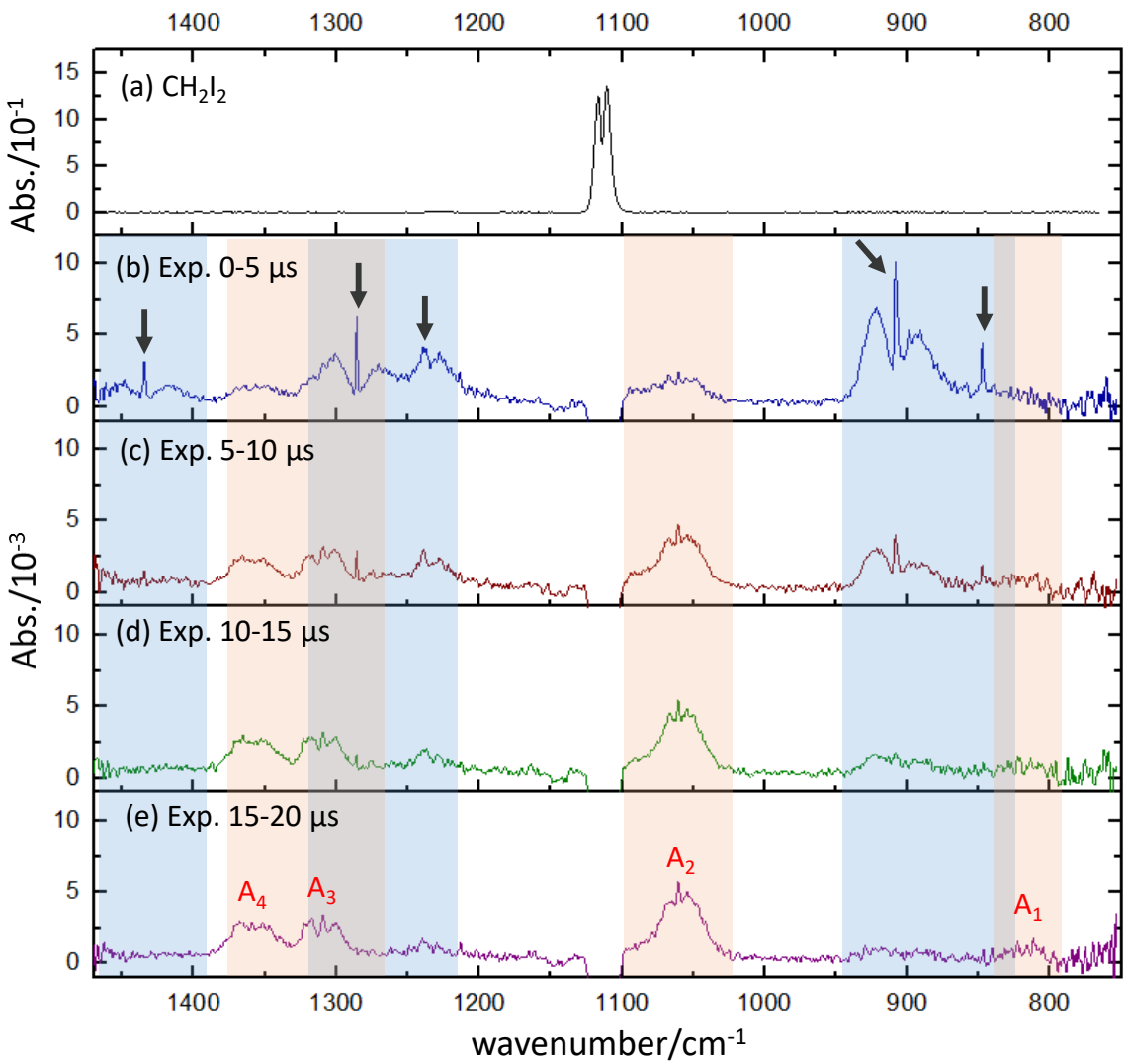
$CH_2I_2/HCl/N_2/O_2$
P_{total} ~ 100 Torr, T = 298 K

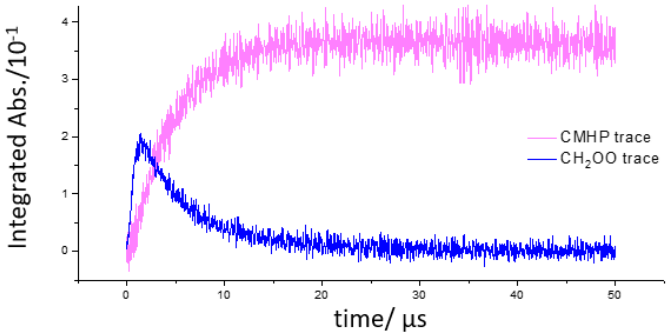
temporal resolution = 4 ns – 12.5 µs
spectral resolution = 0.25 – 2 cm^{-1}



Survey spectra of CH_2OO + HCl at resolution 1 cm^{-1}

P_t = 105 Torr, (CH_2I_2/HCl/O_2/N_2 = 0.15/1/46/54), 298 K
photolysis wavelength: 308 nm





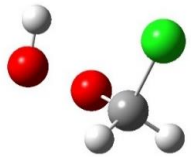
decreasing bands
→ CH_2OO

ν_3	ν_4	ν_5	ν_6	ν_8
1435	1286	1241	908	848

new bands → group A

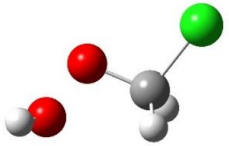
Comparison of observed spectra with predicted stick spectra

C1



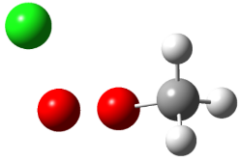
0 kJ/mol

C2

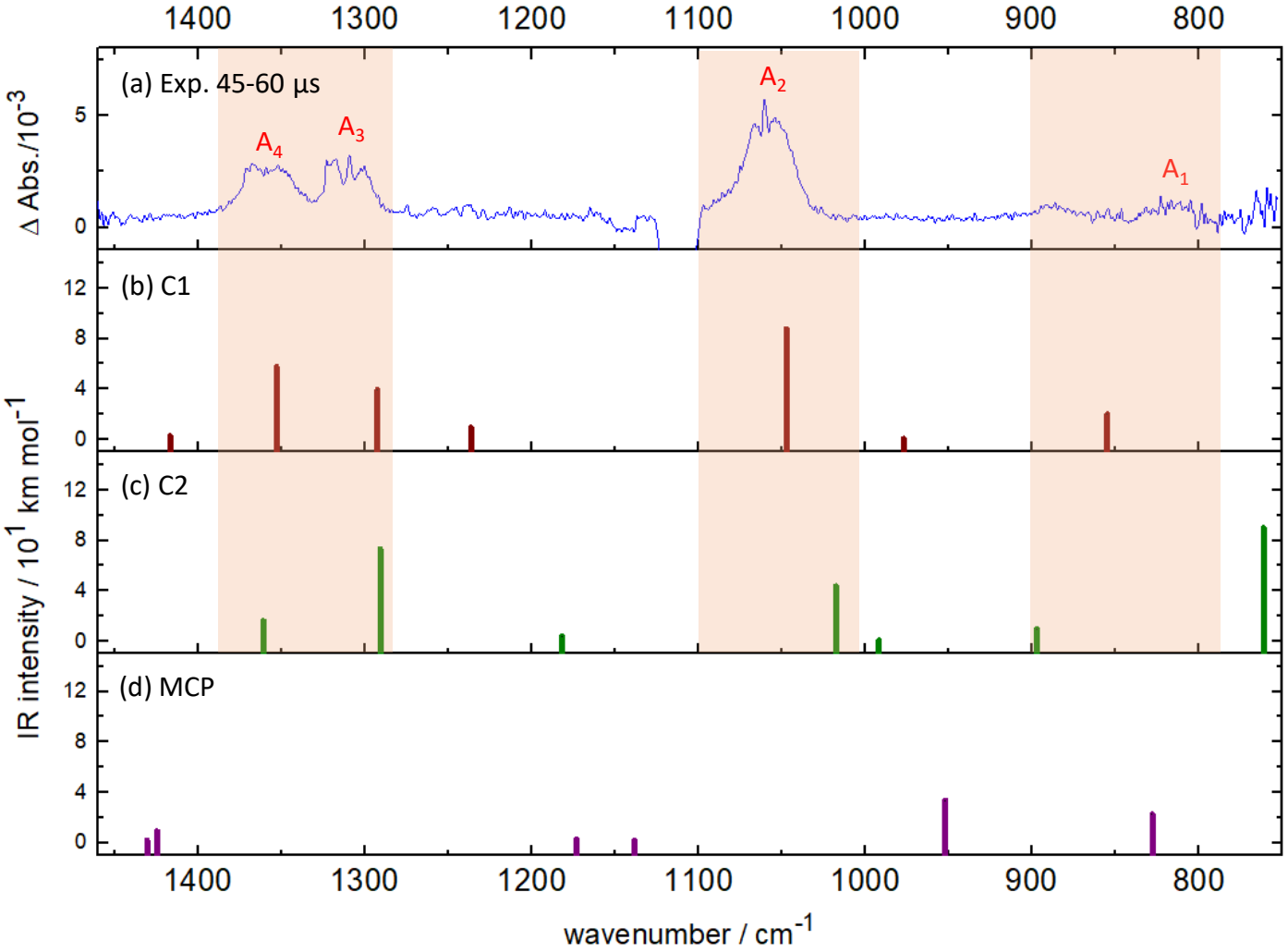


21 kJ/mol

MCP



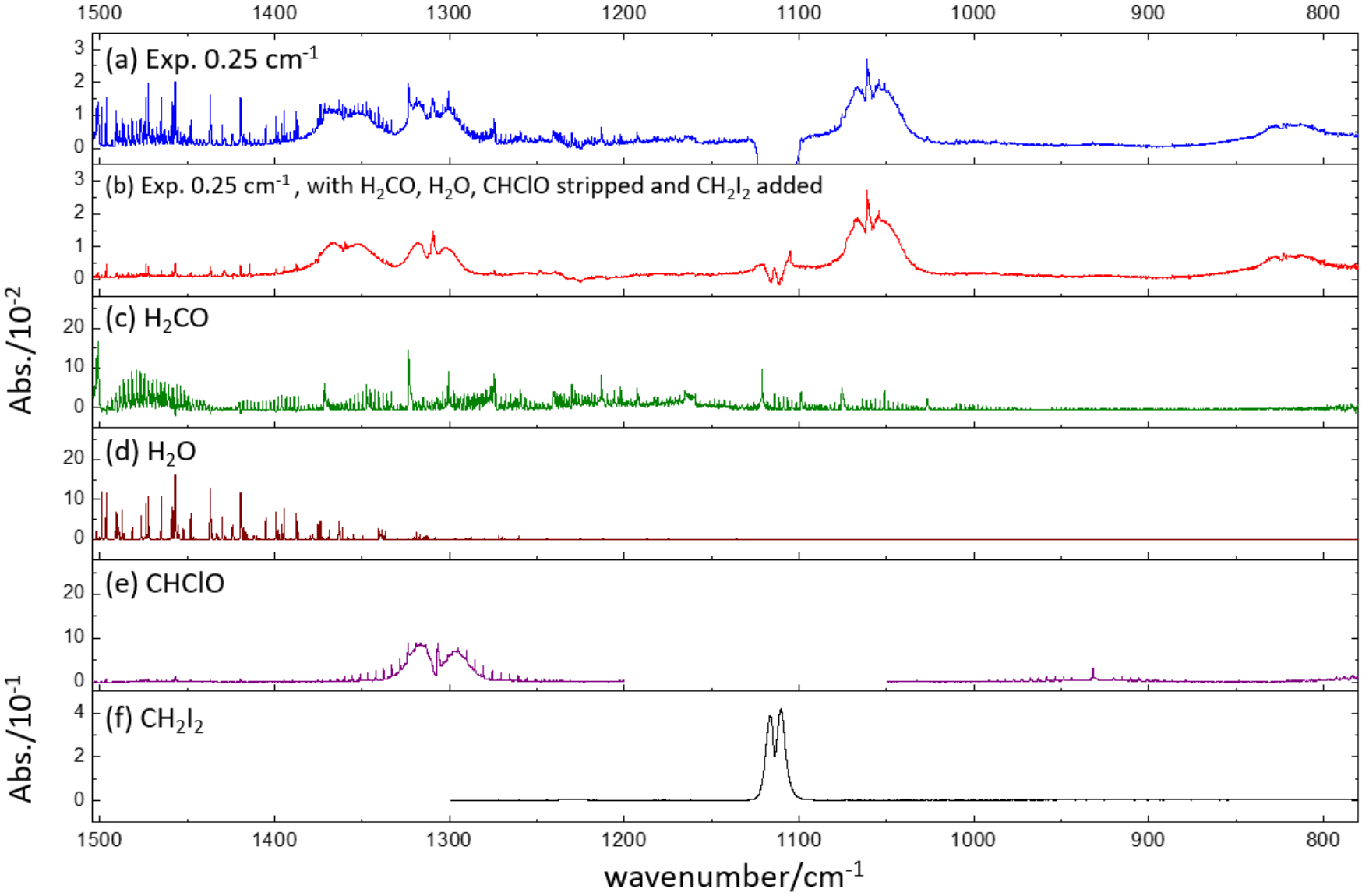
158 kJ/mol



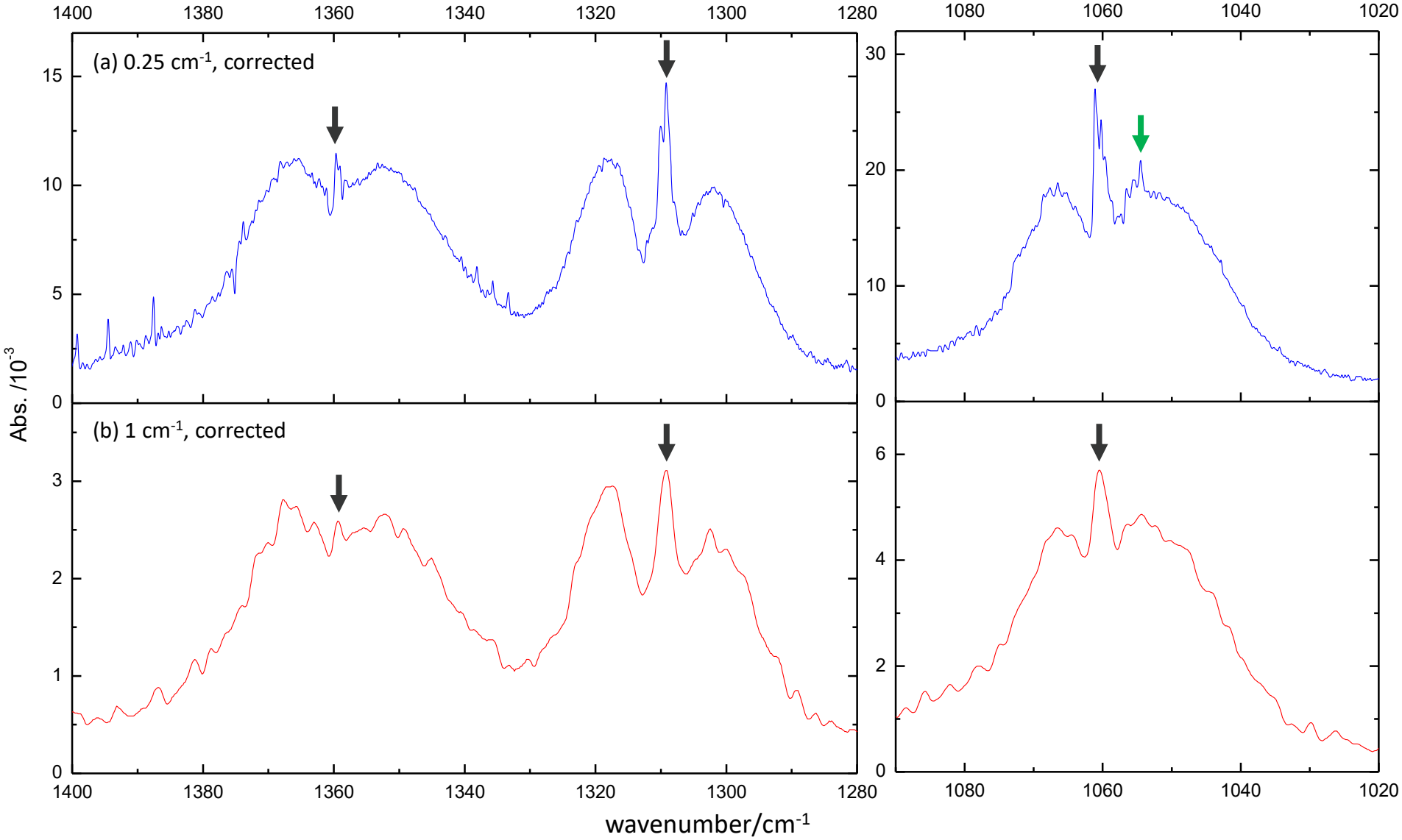
B3LYP/aug-cc-pVTZ
(anharmonic freq.)

C1 and C2 might contribute to the observed spectra.

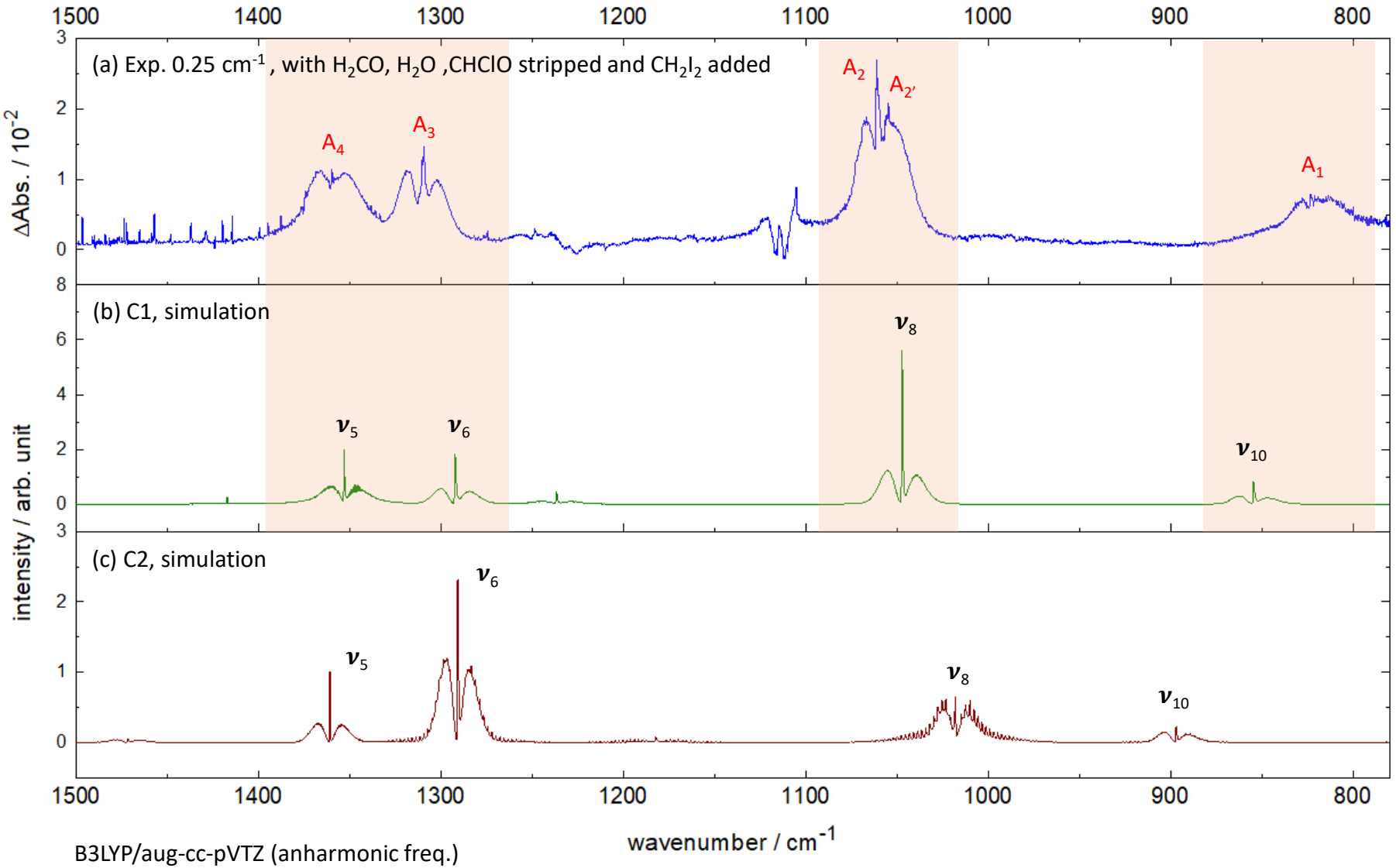
Spectra of CH_2OO + HCl at resolution 0.25 cm^{-1}



Spectra of CMHP at resolution 0.25 cm^{-1}

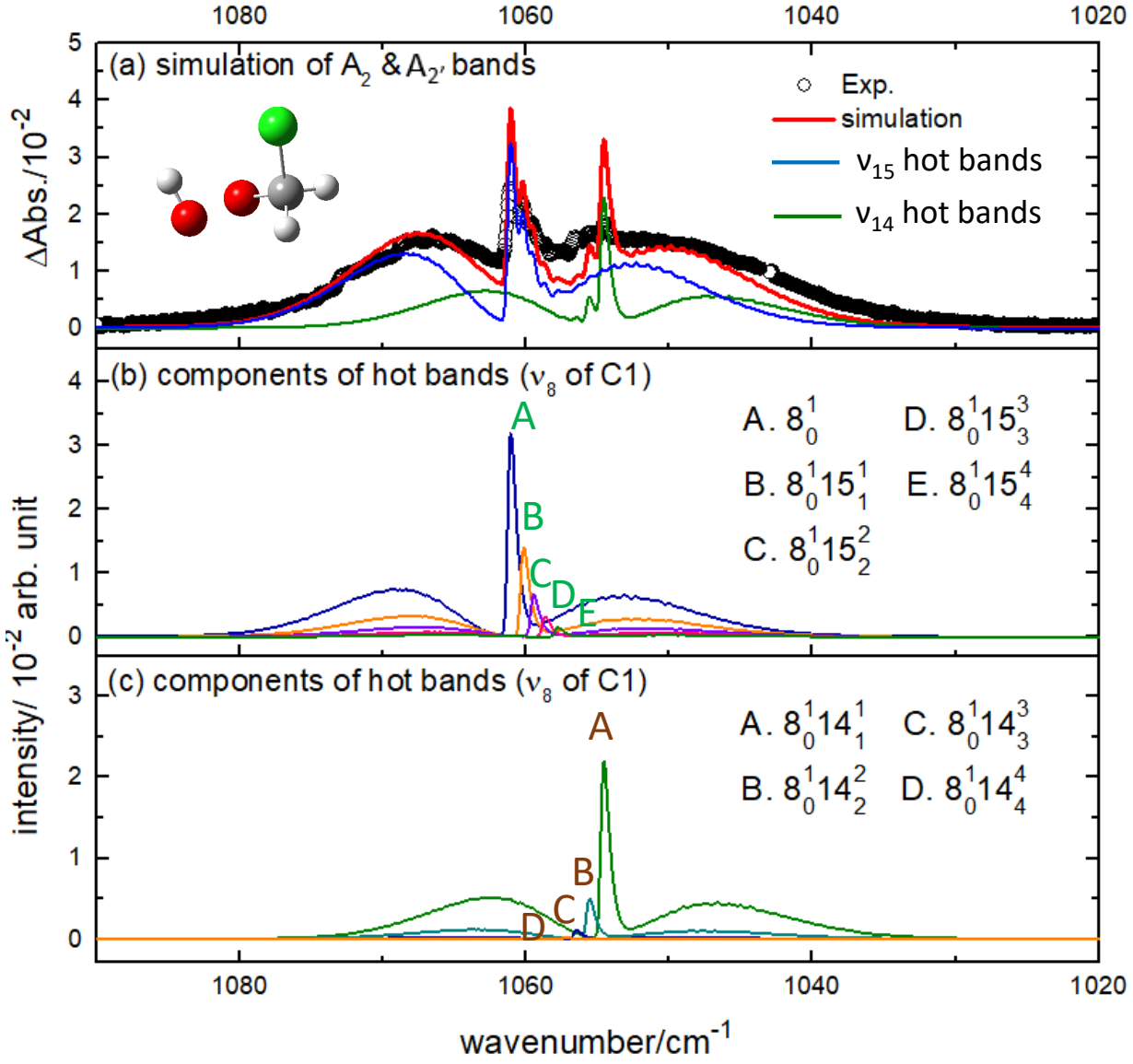


Comparison of observed spectra with simulated spectra



B3LYP/aug-cc-pVTZ (anharmonic freq.)

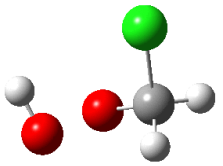
ν_8 mode of CMHP



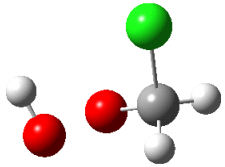
These broad bands might be contributed by **hot bands** from excited levels of the low-energy vibrational mode.

Low energy modes:

Conformer	C1	C1
Mode (ν)	15	14
Anharmonic (cm^{-1})	150	284



ν_{15}

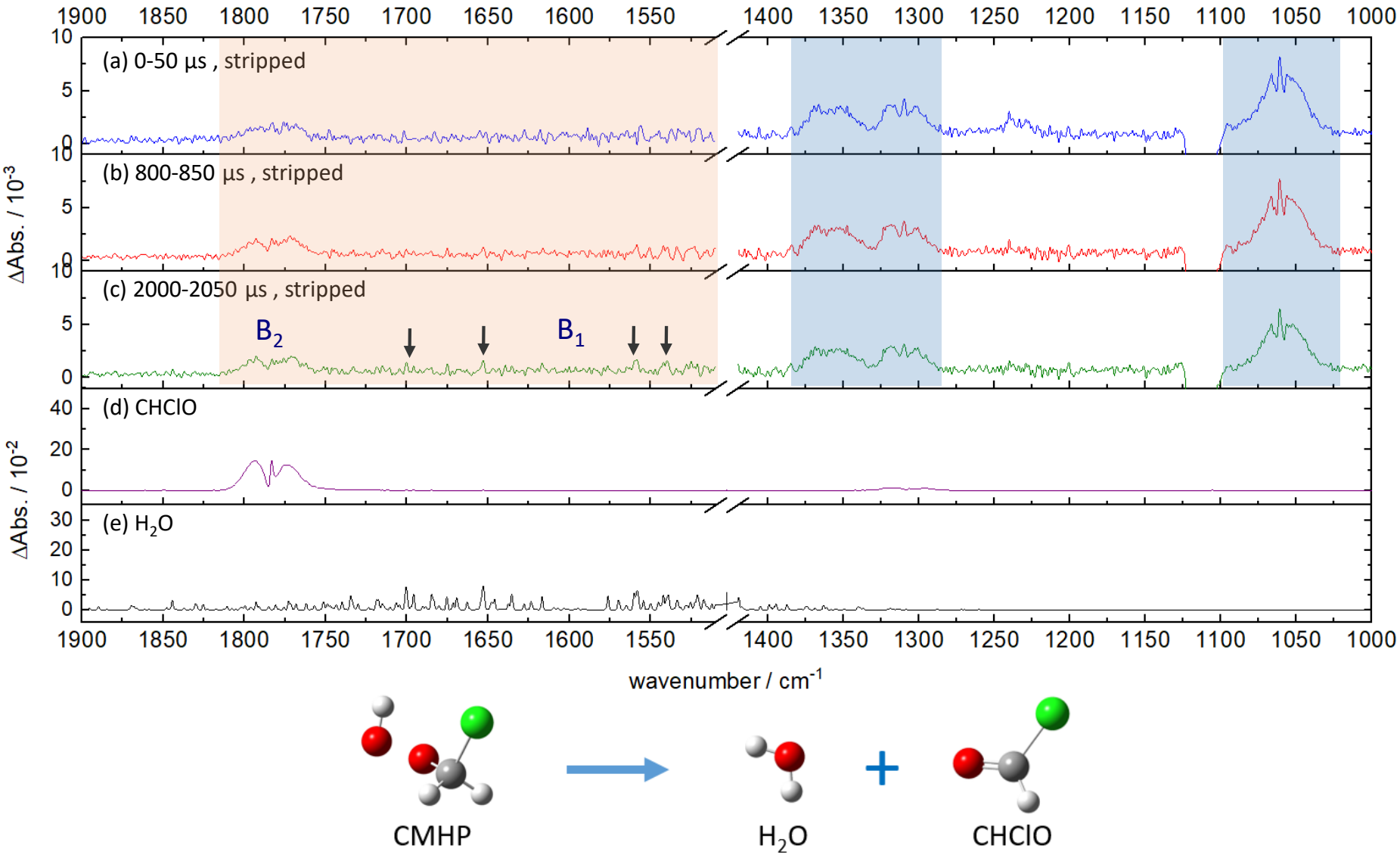


ν_{14}

Assumptions:

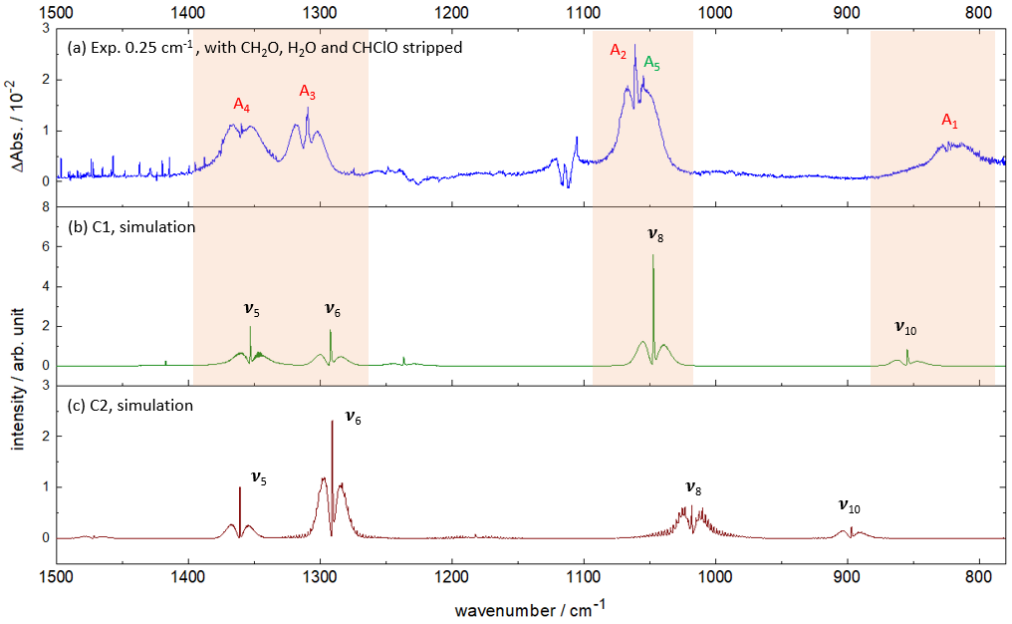
- Rotational contours
  Method: B3LYP/aug-cc-pVTZ
- Boltzmann distributions
- Peak positions (≅equal spacing)

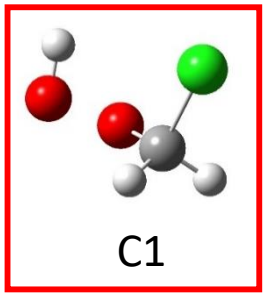
Decomposition of CMHP

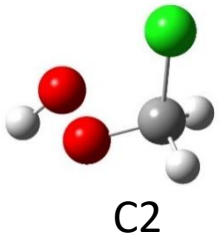


Conclusion

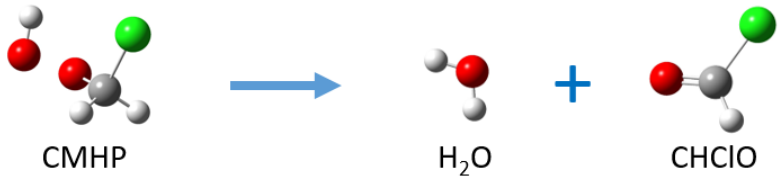
1. Chloromethyl hydroperoxide was produced from CH_2OO + HCl
   - The observed bands are likely due to C1.
   - The band contour is broader than the simulations – contributions of hot bands.



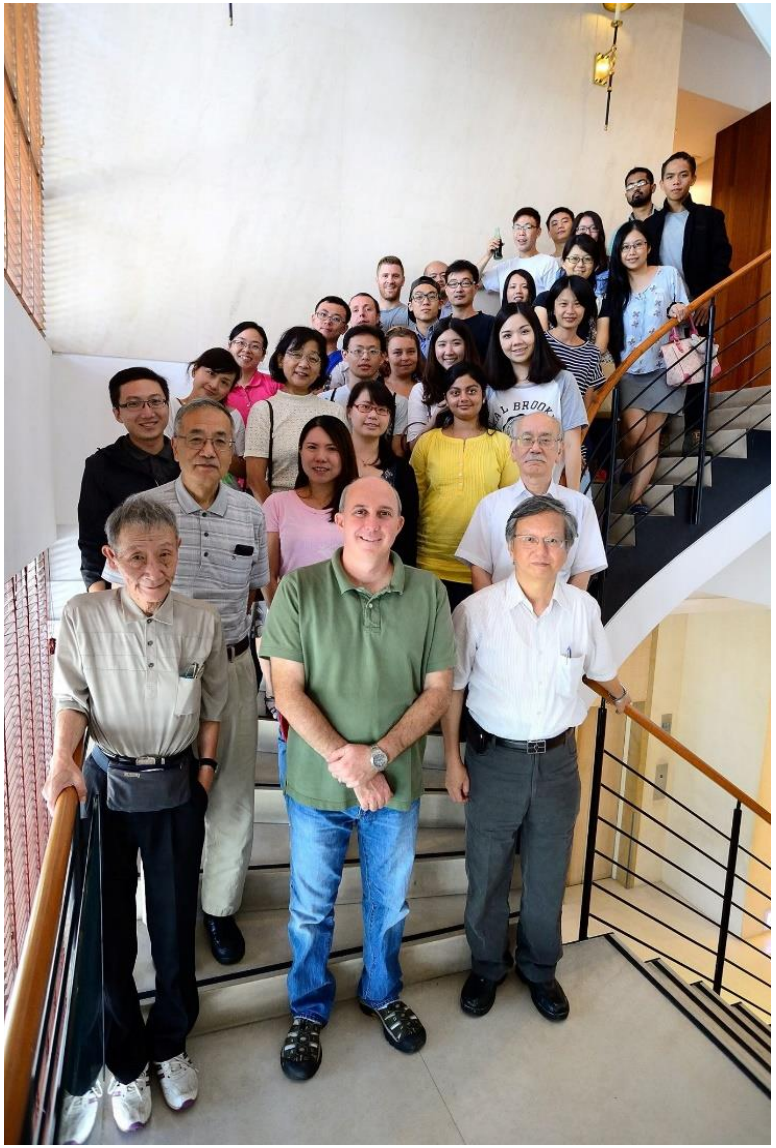




2. At t > 1ms, some CMHP decomposes to CHClO and H_2O .

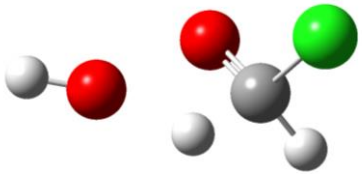


Acknowledgement



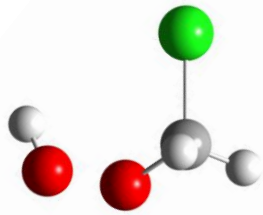
Prof. Yuan-Pern Lee
Prof. Yasuki Endo
Prof. Hiroyuki Matsui
All members in YP's lab

Thanks for your attention!



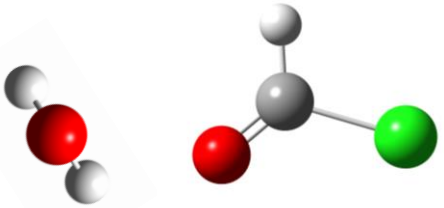
TS

210 kJ/mol



gauche – CMHP (C1)

0 kJ/mol



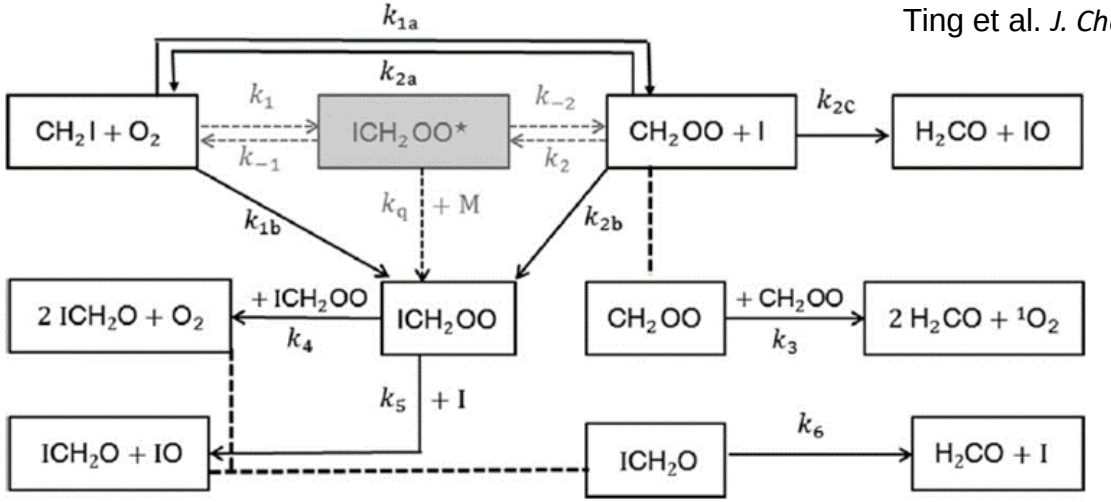
H_2O + CHClO

-252 kJ/mol

B3LYP/aug-cc-pVTZ

Reaction mechanism of $CH_2I + O_2$

Ting et al. *J. Chem. Phys.* **141**, 104308 (2014)



	Reaction/description	Expression[a]	Conditions
k_{1a}	$CH_2I + O_2 \rightarrow CH_2OO + I$	1.5×10^{-12} /{1 + (1.1 ± 0.1) × 10^{-19} [M]}	P ≥ 60 Torr
k_{1a}'	$CH_2I + O_2 \rightarrow CH_2OO + I$	$\beta \times 1.5 \times 10^{-12}$ /{1 + (1.1 ± 0.1) × 10^{-19} [M]}	P < 60 Torr
β	Fraction of survival of CH_2OO at low P, $\beta = k_{1a}'/k_{1a}$	1 − (0.47 ± 0.11)/{1 + (3.2 ± 1.2) × 10^{-18} [M]}[b]	P < 60 Torr
k_{1b}	$CH_2I + O_2 \xrightarrow{M} ICH_2OO$	$1.5 \times 10^{-12} - k_{1a}$	
k_{1c}	$CH_2I + O_2 \rightarrow$ products other than CH_2OO or ICH_2OO	$k_{1a}\,(1-\beta)$	P < 60 Torr
k_{2a}	$CH_2OO + I \rightarrow CH_2I + O_2$	$55\,k_{1a}$	
k_{2b}	$CH_2OO + I \xrightarrow{M} ICH_2OO$	$55\,k_{1b}$	
k_{2c}	$CH_2OO + I \rightarrow H_2CO + IO$	9.0×10^{-12}	
k_3	$CH_2OO + CH_2OO \rightarrow 2\,H_2CO + O_2\,(^1\Delta_g)$	$(8 \pm 4) \times 10^{-11}$	
y	Yield of CH_2OO, $y^{-1} = (k_{1a}' + k_{1b} + k_{1c})/k_{1a}' = (k_{1a} + k_{1b})/k_{1a}'$	$y^{-1} = (1.24 \pm 0.03) + (9.13 \pm 0.33) \times 10^{-20}$ [M], M = O_2 or N_2	

Table: CMHP (C1)

mode	harmonic	anharmonic	intensity
1	3717	3538	35
2	3169	3022	1
3	3091	2970	9
4	1456	1416	2
5	1390	1353	57
6	1322	1292	39
7	1267	1236	9
8	1078	1047	87
9	996	977	1
10	877	854	20
11	664	654	130
12	494	484	22

mode	harmonic	anharmonic	intensity
13	365	359	7
14	260	284	107
15	143	149	19

Table: CMHP (C2)

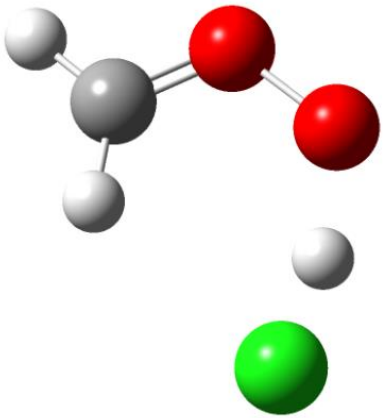
mode	harmonic	anharmonic	intensity
1	3747	3565	55
2	3125	2976	9
3	3058	2885	20
4	1510	1471	2
5	1370	1360	16
6	1340	1290	73
7	1208	1181	3
8	1050	1017	43
9	1003	991	0
10	920	897	9
11	781	761	89
12	398	391	1

mode	harmonic	anharmonic	intensity
13	271	317	6
14	240	136	106
15	92	84	3

Table: CH_2OO-HCl complex

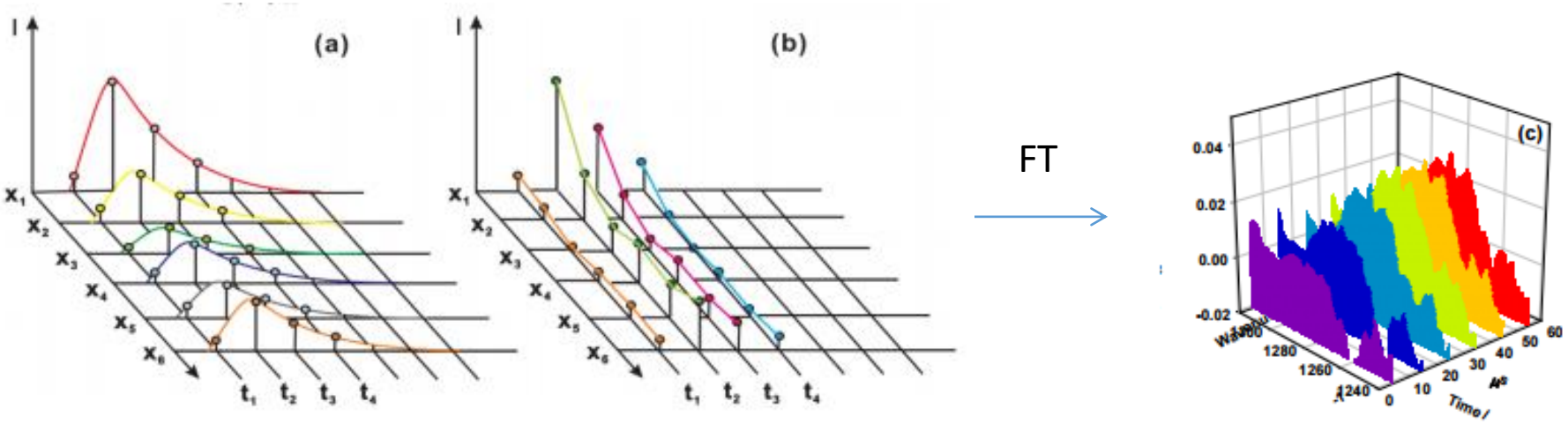
mode	harmonic	intensity
1	3265	3
2	3121	4
3	1632	1536
4	1578	12
5	1423	48
6	1244	6
7	1035	30
8	1023	210
9	850	97
10	755	20
11	663	4
12	509	17

mode	harmonic	intensity
13	230	198
14	175	8
15	63	2



Step-scan FTIR

- The moving mirror scans discontinuously and stops at specific points defined by the zero crossing points of the He-Ne laser.



(a) is the temporal profile at different position, after rearrangement of (a), (b) shows interferograms at different time. And after fourier transform, the time-resolved spectrum can be obtained.

Hot bands

$$E_v = \omega_e (v + ½) - \omega_e x_e (v + ½)^2$$

ν_{15} of C1

level	population
0	1
1	0.49
2	0.23
3	0.11
4	0.05
5	0.02
6	0.01

ν_{14} of C1

level	population
0	1
1	0.23
2	0.05
3	0.01
4	
5	
6	

ν_5 &ν_6 modes

ν_5 of C1

ν_5	1359.9
A’/A	0.9995
B’/B	0.9978
C’/C	0.9982
a-type	0.33
b-type	0.6
c-type	0.07

ν_6 of C1

ν_6	1309.4
A’/A	0.9975
B’/B	0.9985
C’/C	0.9980
a-type	0.89
b-type	0.07
c-type	0.04

Reaction of Cl and other atmospheric species

- $CH_2OO + NO_2 \rightarrow H_2CO + NO_3$ $k = (7 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}
- $CH_2OO + SO_2 \rightarrow H_2CO + SO_3$ $k = (3.8 - 4.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}
- $CH_2OO + (H_2O) \rightarrow HOCH_2OOH + H_2O$ $k = (4.0 - 6.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}

Welz et al., *Science* **335**, 204 (2012).

Liu et al., *J. Phys. Chem. A* **118**, 741 (2014).

Sheps et al., *J. Phys. Chem. Lett.* **4**, 4201 (2013).

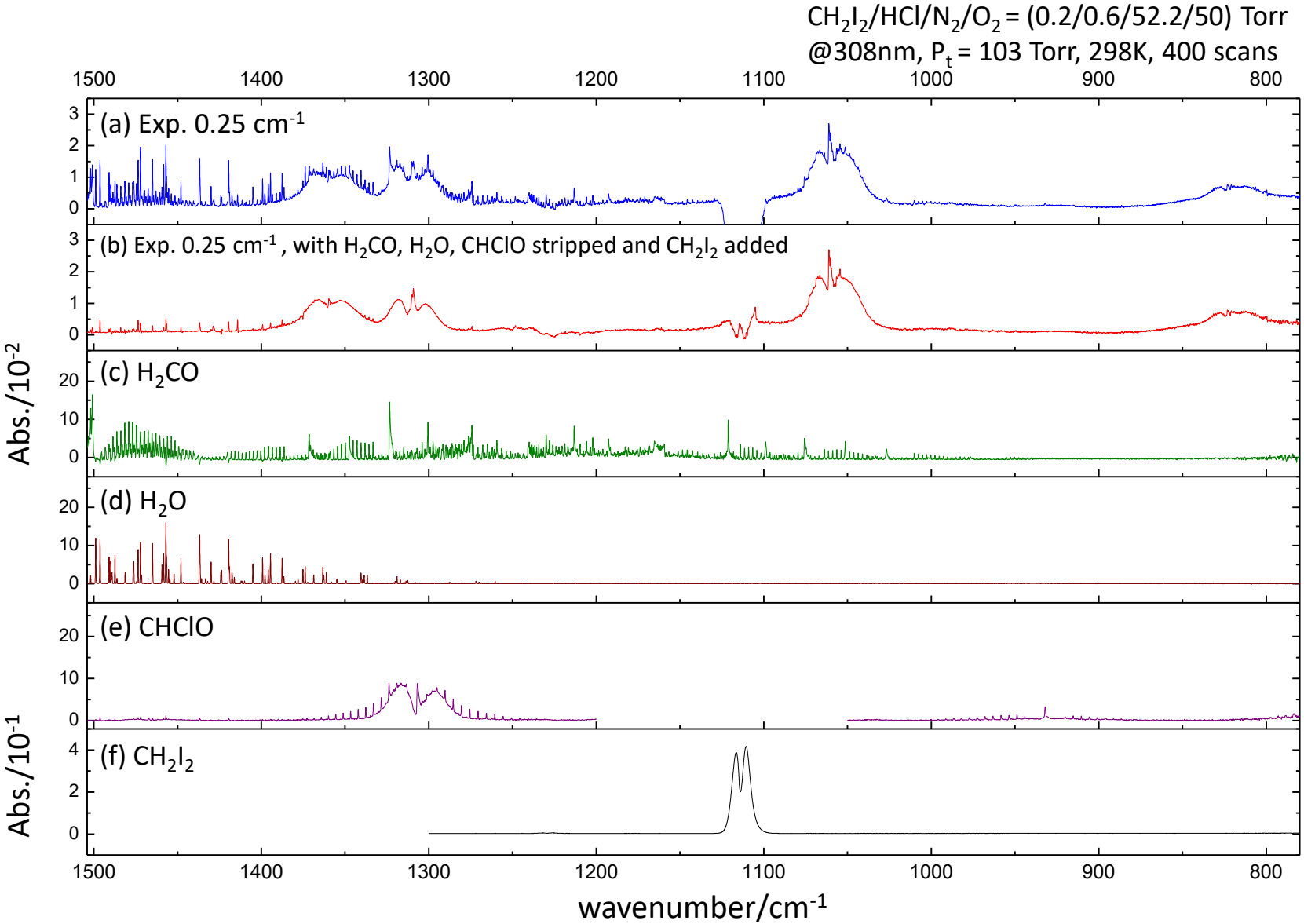
Chhantyal-pun et al., *Phys. Chem. Chem. Phys.* **17**, 3617 (2015).

Stone et al, *Phys. Chem. Chem. Phys.* **16**, 1139 (2014).

Lewis et al., *Phys. Chem. Chem. Phys.* **17**, 4859 (2015).

Chao et al., *Science* **347**, 751 (2015).

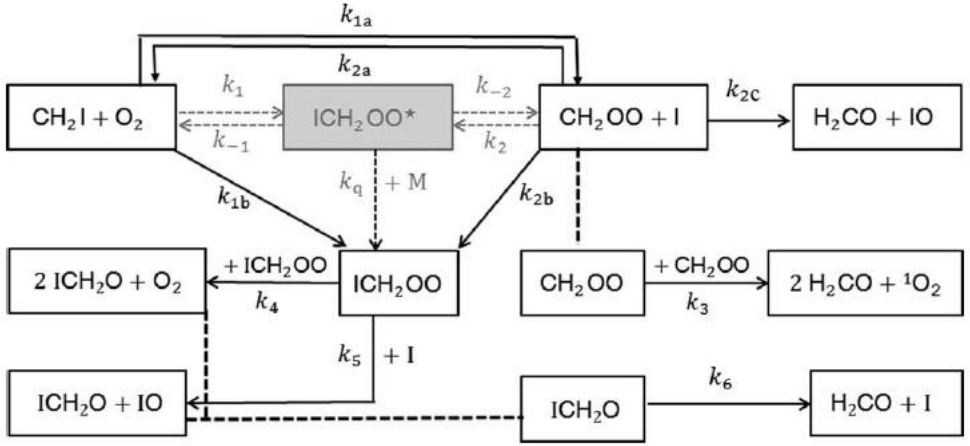
Spectra of CH_2OO+HCl at 0.25 cm^{-1} resolution



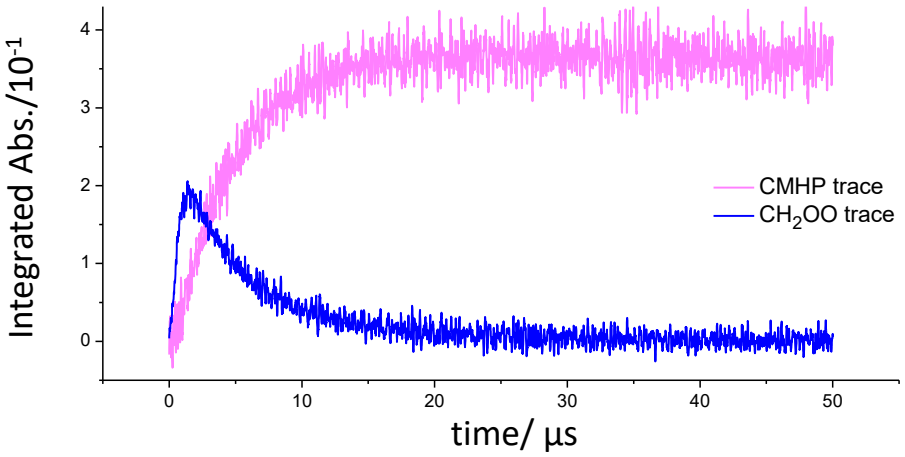
Kinetic of CH_2OO + HCOOH

CI mechanism:

$CH_2I + O_2 \rightarrow CH_2OO + I$	k1a
$CH_2I + O_2 \rightarrow CH_2IOO$	k1b
$CH_2OO + I \rightarrow CH_2I + O_2$	k2a
$CH_2OO + I \rightarrow CH_2IOO$	k2b
$CH_2OO + I \rightarrow CH_2O + IO$	k2c
$2CH_2OO \rightarrow 2CH_2O + O_2$	k3
$2CH_2IOO \rightarrow 2ICH_2O + O_2$	k4
CH2IOO + I → ICH2O + IO	k5
$ICH_2O \rightarrow CH_2O + I$	k6
$CH_2OO \rightarrow$ CMHP	k



Ting et al. *J. Chem. Phys.* **141**, 104308 (2014)



$CH_2I + O_2 \xrightarrow{k_1} CH_2OO$

$CH_2OO + HCl \xrightarrow{k_2} CMHP$

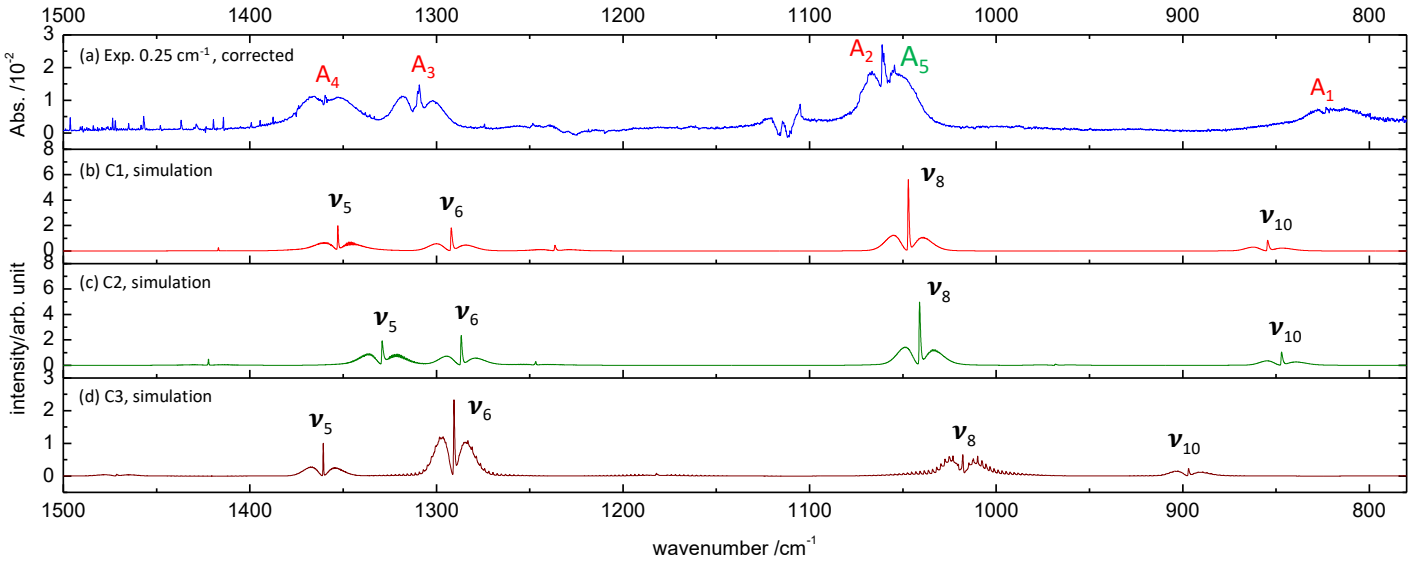
pseudo-first order condition:

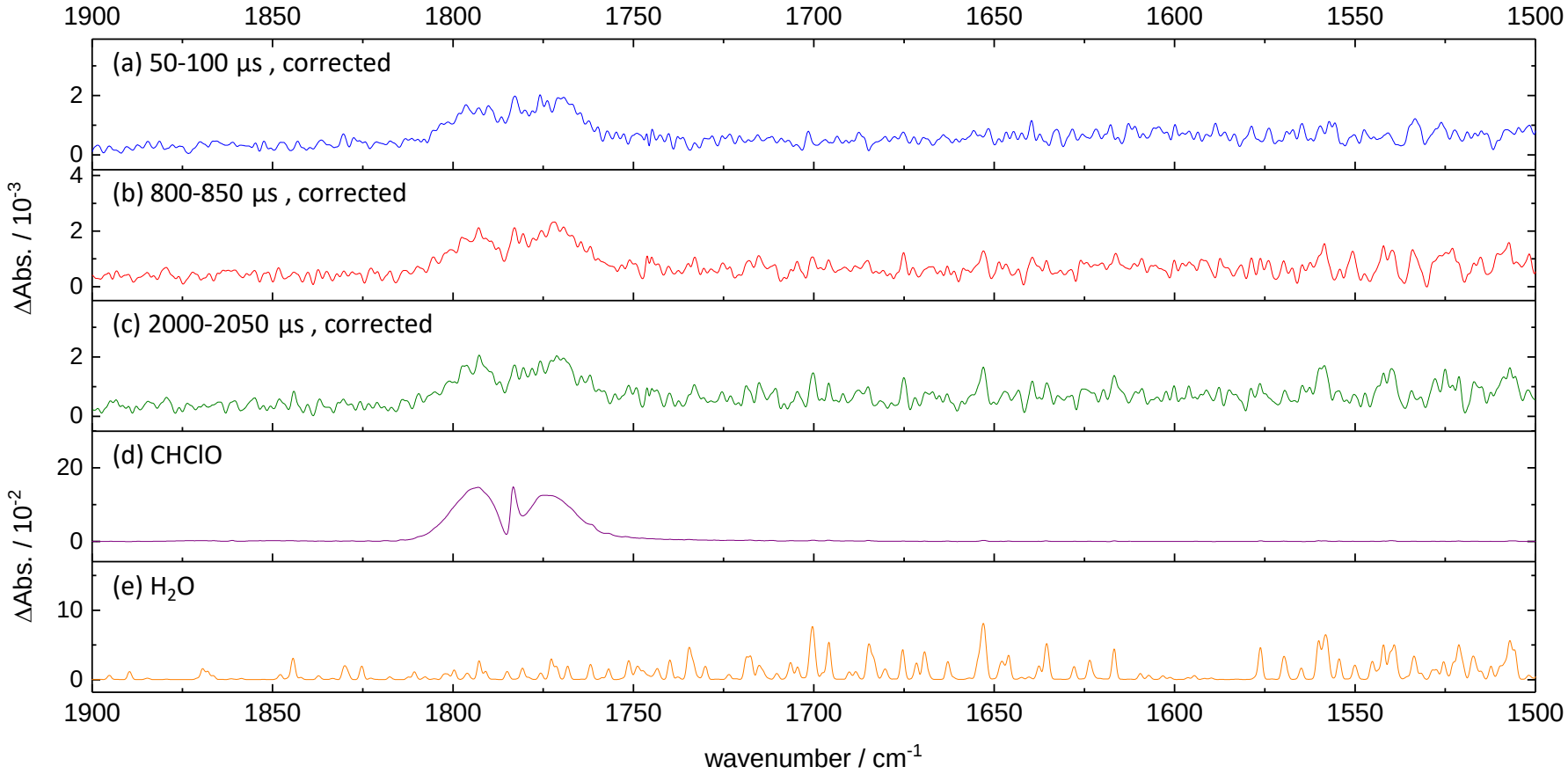
$CH_2I \xrightarrow{k_a} CH_2OO \xrightarrow{k_b} CMHP$

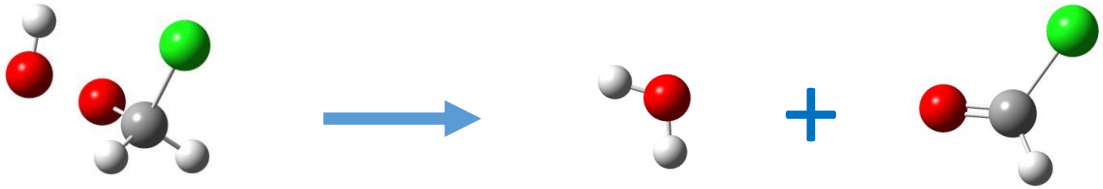
$$[CH_2OO] = \frac{k_a}{k_b - ka}\left(e^{-kat} - e^{-kbt}\right)[CH_2I]_0$$

$k_a = k_1[O_2] = 1740000\ s^{-1}$

$K_b = k_2[HCl]$


(a) Exp. 0.25 cm-1, corrected
A4
A3
A2
A5
A1
(b) C1, simulation
(c) C2, simulation
(d) C3, simulation
ν5
ν6
ν8
ν10
Abs. /10-2
intensity/arb. unit
wavenumber /cm-1
1500
1400
1300
1200
1100
1000
900
800


(a) 50-100 µs , corrected
(b) 800-850 µs , corrected
(c) 2000-2050 µs , corrected
(d) CHClO
(e) H2O
ΔAbs. / 10-3
ΔAbs. / 10-2
wavenumber / cm-1
1900
1850
1800
1750
1700
1650
1600
1550
1500


CMHP
H2O
CHClO

Important reactions of CH_2OO (298 K)

$CH_2OO \rightarrow HCO + OH$	$k = 0.02\ s^{-1}$ (theory)
$CH_2OO \rightarrow H_2CO_2$ (dioxirane)	$k = 1.2 \times 10^{-12}\ s^{-1}$ (theory)
$CH_2OO \rightarrow CO + H_2O$	$k = 6 \times 10^{4}\ s^{-1}$
$CH_2OO + CH_2OO \rightarrow 2\ CH_2O + O_2$	$k = (8 \pm 4) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$
$CH_2OO + NO_2 \rightarrow H_2CO + NO_3$	$k = (7.0 \pm 1.5) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$
$CH_2OO + SO_2 \rightarrow H_2CO + SO_3$	$k = (3.8 - 4.1) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$
$CH_2OO + (H_2O)_2 \rightarrow$ product	$k = (4.0 - 6.5) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$
$CH_2OO + HCOOH \rightarrow$ product	$k = (1.1 \pm 0.1) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$

Sheps et al., *J. Phys. Chem. Lett.* **4**, 4201 (2013).
Liu et al., *J. Phys. Chem. A* **118**, 741 (2014).
Welz et al., *Science* **335**, 204 (2012).
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Lewis et al., *Phys. Chem. Chem. Phys.* **17**, 4859 (2015).
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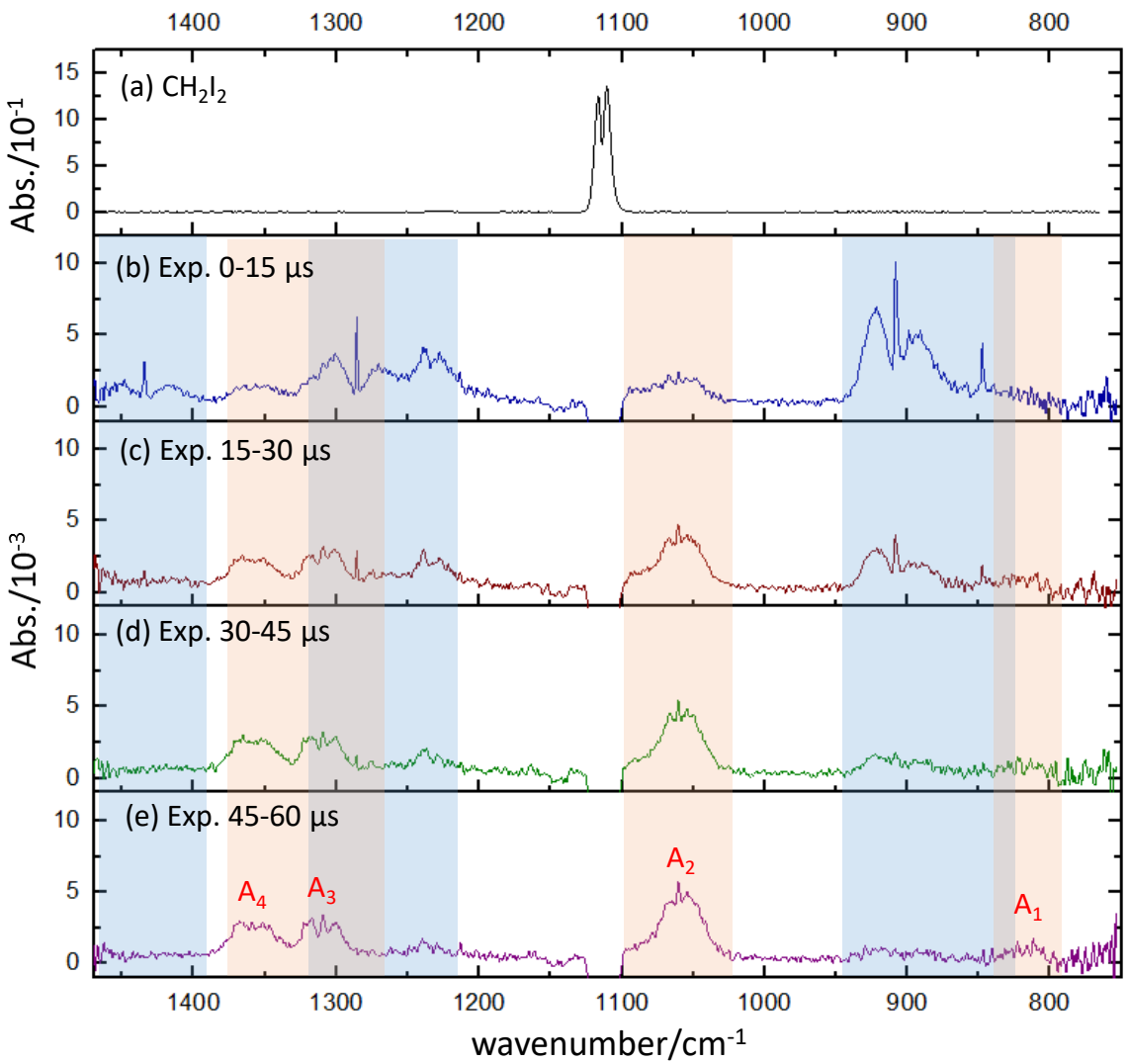
Chhantyal-pun et al., *Phys. Chem. Chem. Phys.* **17**, 3617 (2015).

Survey spectra of CH_2OO + HCl at resolution 1 cm^{-1}

P_t = 105 Torr, (CH_2I_2/HCl/O_2/N_2 = 0.15/1/46/54), 298 K
photolysis wavelength: 308 nm

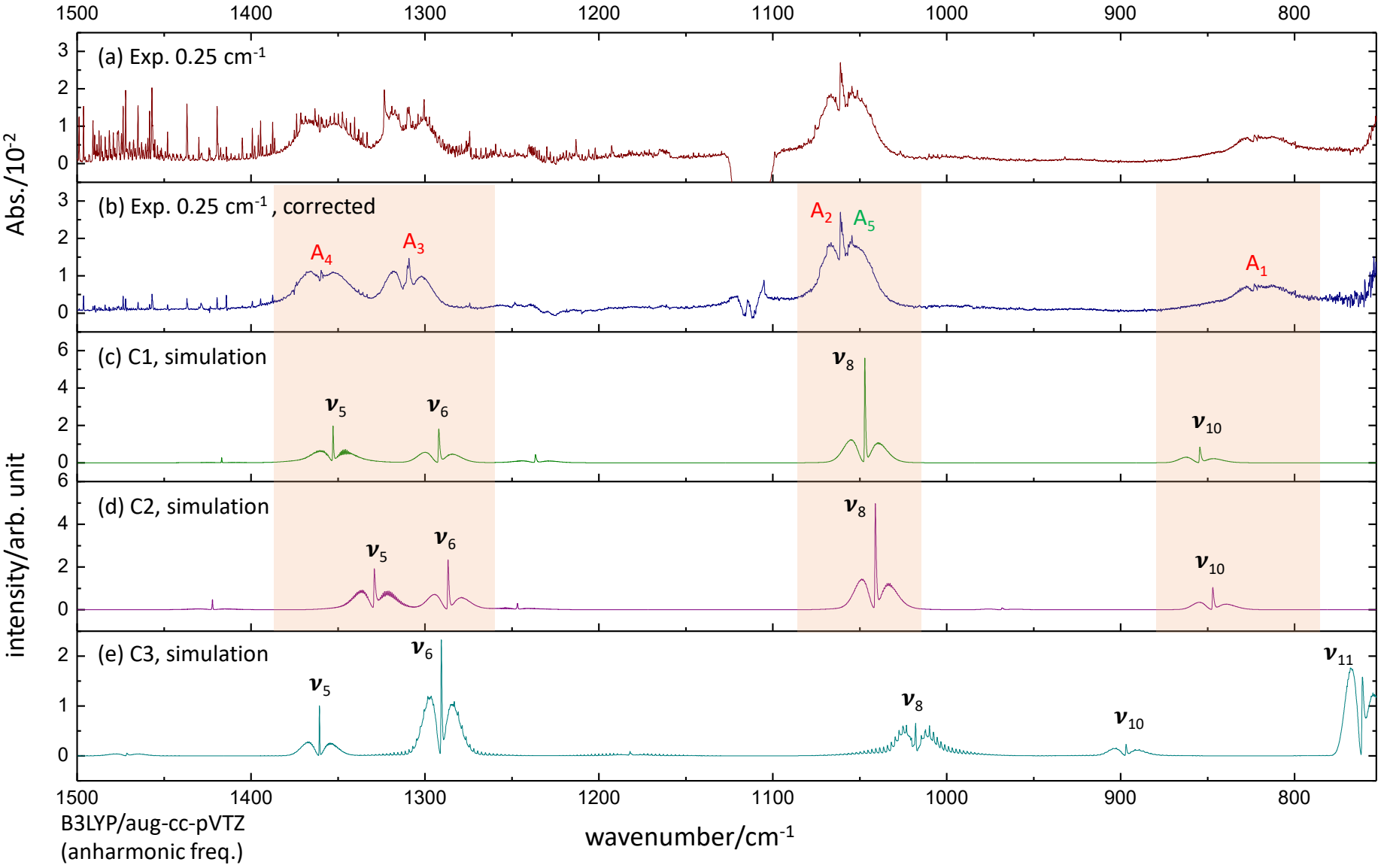


decreasing bands
→ CH_2OO

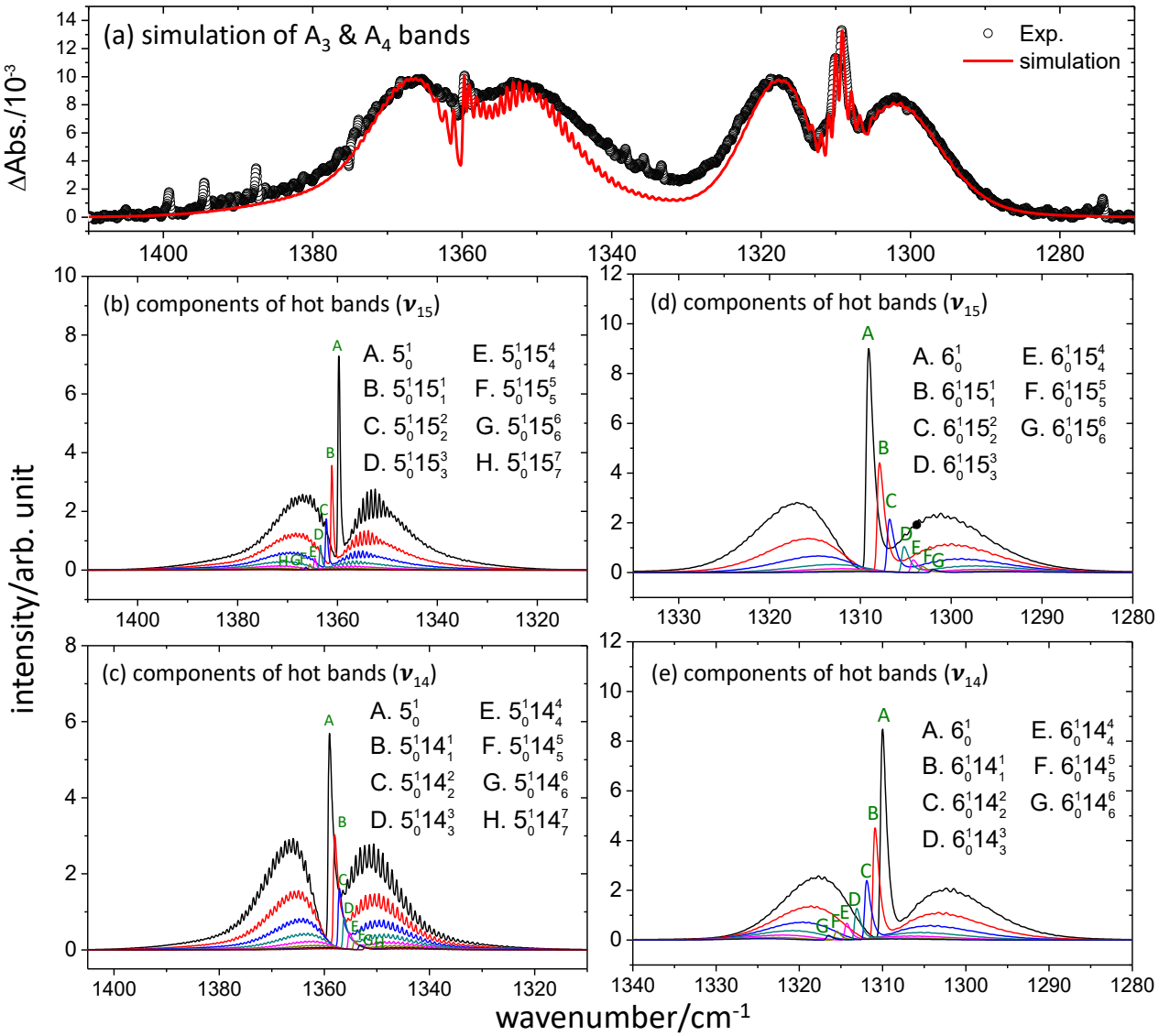
ν_3	ν_4	ν_5	ν_6	ν_8
1435	1286	1241	908	848

new bands → group A

Comparison of observed spectra with simulated spectra



ν_5 & ν_6 modes of CMHP



These broad bands might be contributed by **hot bands** from excited levels of the low-energy vibrational mode.

Low energy modes:

Conformer	C1	C1
Mode (ν)	15	14
Anharmonic (cm^{-1})	150	284

Assumptions:

- Rotational contours
  Method: B3LYP/aug-cc-pVTZ
- Boltzmann distributions
- Peak positions (≅equal spacing)