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## Supplementary information

### **Kinetics of CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub> (HFE-263fb2), CHF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> (HFE-374pcf), and CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> (HFE-365mcf3) with OH radicals, IR absorption cross sections, and global warming potentials**

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## 34 IR absorption cross sections of HFEs

35 As Figure S3 shows, even though the differences in the literature peak IR  
36 absorption cross sections  $\sigma_{\bar{\nu},max}$  presented in Table S6, are not huge, a noticeable  
37 difference for HFE-263fb2 ( $\text{CF}_3\text{CH}_2\text{OCH}_3$ ) and for HFE-365mcf3 ( $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$ ) is  
38 observed. The IR spectra from Oyaro et al. (2004, 2005) are systematically lower than  
39 those from Østerstrøm et al. (2012) and Thomsen et al. (2011). Moreover, note that the  
40 IR spectrum reported by Thomsen et al. (2011) presents a zig-zag noise in the whole  
41 spectrum. For HFE-374pcf ( $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$ ), the only IR spectrum available in the  
42 literature is that from Oyaro et al. (2004). As these authors systematically report lower IR  
43 absorption cross sections, a further study is worth it.

44

## 45 Radiative efficiencies and global warming potentials

46 The  $f_\tau$  factor is defined as:

$$47 \quad f_\tau = \frac{a\tau^b}{1+c\tau^d} \quad (\text{ES1})$$

48 where  $a$ ,  $b$ ,  $c$ , and  $d$  are constants with values of 2.962, 0.9312, 2.994, and 0.9302,  
49 respectively (Hodnebrog et al. (2013; 2020)). As the OH-reaction is usually the most  
50 important degradation route for atmospheric pollutants,  $\tau$  is commonly expressed as  $\tau_{\text{OH}}$ .

51 REs of  $\text{CF}_3\text{CH}_2\text{OCH}_3$ ,  $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$ , and  $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$  were  
52 calculated from equation ES2 using the radiative efficiency (for a 0–1 ppb increase in  
53 mixing ratio) per unit cross section ( $F^\sigma$  in  $\text{W m}^{-2} \text{ cm molecule cm}^{-2}$ ) at a  $1 \text{ cm}^{-1}$  resolution  
54 reported in the updated Oslo line-by-line radiative transfer model that now accounts for  
55 stratospheric temperature adjustment (Shine and Myhre, 2020).

$$56 \quad RE_i = f_\tau \times \sum_{500\text{cm}^{-1}}^{3000\text{cm}^{-1}} \sigma_{\bar{\nu},i} F^\sigma \quad (\text{ES2})$$

57 As in our previous works (Blázquez et al., 2017; Antiñolo et al., 2017; González  
58 et al., 2016; Jiménez et al., 2016; González et al., 2015), GWPs of HFEs for a time horizon  
59 of 100 years ( $GWP_i(100 \text{ yrs})$ ) were calculated by the following expression, according to  
60 Hodnebrog et al. (2013; 2020):

$$61 \quad GWP_i(100 \text{ yrs}) = \frac{AGWP_i(100 \text{ yrs})}{AGWP_{\text{CO}_2}(100 \text{ yrs})} \quad (\text{ES3})$$

62 where  $AGWP_{CO_2}(100\text{ yrs})$  is the absolute GWP of  $CO_2$  with value of  $8.064 \times 10^{-14}$  (in  
63  $Wm^{-2}yr$  ( $kg\ CO_2$ ) $^{-1}$ ) and  $AGWP_i(100\text{ yrs})$  is the absolute GWP for the HFE at the same  
64 time horizon, which is defined as:

$$65 \quad AGWP_i(100\text{ yrs}) = RE_i \times \tau_{OH} \times \left[ 1 - \exp\left(-\frac{100\text{ yrs}}{\tau_{OH}}\right) \right] \quad (ES4)$$

66 where  $\tau_{OH}$  and  $RE_i$  are expressed in years and  $W\ m^{-2}$  ( $kg\ HFE$ ) $^{-1}$ , respectively.

67 In Table S7,  $\tau_{OH}$ , REs, and  $GWP(100\text{ yrs})$  for some HFCs with the same number  
68 of C-F bonds of the investigated HFEs are also presented. It is clear that the presence of  
69 the ether group decreases  $\tau_{OH}$  from several years for HFCs to 2-3 weeks for HFEs  
70 (Hodnebrog et al., 2020). If we compare the RE of HFE-263fb2 with that of the  
71 corresponding HFC,  $CF_3CH_2CH_3$  (HFC-263fb), a noticeable decrease is observed  
72 (Hodnebrog et al., 2020). This, together with a lifetime of 1.2 years, makes the  $GWP(100$   
73  $\text{ yrs})$  be two orders of magnitude higher than that for HFE-263fb2. The analogous HFC of  
74  $CHF_2CF_2CH_2OCH_3$  and  $CF_3CF_2CH_2OCH_3$  are  $CHF_2CF_2CH_2CH_3$  and  $CF_3CF_2CH_2CH_3$ ,  
75 respectively. To our knowledge, their OH-kinetics and IR absorption cross sections have  
76 not been reported to date. For that reason, the RE and  $GWP(100\text{ yrs})$  of  
77  $CHF_2CF_2CH_2OCH_3$  and  $CF_3CF_2CH_2OCH_3$  are compared with those of  $CHF_2CHF_2$   
78 (HFC-134), and  $CHF_2CF_3$  (HFC-125), and  $CF_3CF_2CH_3$  (HFC-245cb), which have 4 and  
79 5 C-F bonds (Hodnebrog et al., 2020). The RE of HFC-134 is more than 6 times higher  
80 than that for HFE-374pcf, while the decrease in  $GWP(100\text{ yrs})$  is huge, from 1330 to 0.46.  
81 Similarly, the RE for HCF-125 and HFC-245cb are more than 6 times higher than that  
82 for HFE-365mcf3. In combination with the large atmospheric lifetime (30 and 39.9  
83 years), their  $GWP(100\text{ yrs})$  are more than three orders of magnitude higher (6793 and  
84 8259) (Hodnebrog et al., 2020) than that of HFE-365mcf3.

85

SUPPLEMENTARY TABLES

**Table S1.** Experimental conditions and individual rate coefficients ( $\pm 2\sigma$ ) for the OH + CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub> reaction.

$T / \text{K}$	$p_{\text{T}} / \text{Torr}$	$f / 10^{-2}$	$F_{\text{R}} / \text{sccm}$	$F_{\text{H}_2\text{O}_2/\text{He}} / \text{sccm}$	$F_{\text{He}} / \text{sccm}$	$[\text{CF}_3\text{CH}_2\text{OCH}_3] / 10^{15} \text{ molecules cm}^{-3}$	$k^{\text{a}}-k^{\text{b}}_0 / \text{s}^{-1}$	$k_{\text{OH}}(T) / 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
263	50	3.65	9.4 – 85.1	12.3	366.6 – 458.9	1.33 – 12.3	760 – 7040	5.87 ± 0.32
	50	1.49	10.3 – 94.0	12.3	366.6 – 458.9	0.60 – 5.41	311 – 3391	6.38 ± 0.27
	250	1.59	1.5 – 12.3	11.3	448.3 – 460.7	0.46 – 3.81	383 – 2494	6.53 ± 0.38
	250	1.59	1.5 – 13.7	11.3	446.9 – 460.7	0.46 – 4.23	343 – 2745	6.42 ± 0.30
	500	1.59	1.5 – 13.7	12.3	445.0 – 458.9	0.93 – 8.48	584 – 4970	6.14 ± 0.41
	500	3.65	1.4 – 12.4	12.3	457.5 – 458.9	1.93 – 17.6	1394 – 10220	5.58 ± 0.21
268	50	1.49	10.3 – 47.5	12.3	412.8 – 458.9	0.32 – 2.69	206 – 1700	6.18 ± 0.51
	50	3.97	9.2 – 83.3	12.3	366.6 – 458.9	1.40 – 12.9	873 – 7170	5.62 ± 0.35
	50	3.97	9.2 – 75.1	12.3	375.9 – 458.9	1.40 – 11.6	1011 – 7502	6.49 ± 0.40
278	50	1.50	10.3 – 84.7	4.0	385.1 – 468.1	0.57 – 4.65	375 – 3374	6.95 ± 0.44
	50	3.99	9.2 – 83.2	4.0	375.9 – 468.1	1.35 – 12.5	1021 – 7707	6.32 ± 0.32
288	50	1.50	10.3 – 93.9	8.6	371.2 – 463.5	0.55 – 4.99	573 – 3593	6.86 ± 0.37
	50	3.99	9.2 – 83.2	8.6	371.2 – 463.5	1.30 – 12.0	1027 – 7911	6.53 ± 0.18
298	50	3.98	9.2 – 83.2	7.6	371.2 – 463.5	1.26 – 11.6	996 – 7737	6.46 ± 0.24
	50	3.32	9.6 – 86.9	4.0	375.9 – 468.1	1.09 – 10.0	748 – 6949	7.11 ± 0.20
	250	3.98	0.9 – 8.2	15.8	449.7 – 458.9	0.63 – 5.55	452 – 4112	7.46 ± 0.40
	250	3.90	1.3 – 12.2	11.3	446.9 – 460.7	0.90 – 8.20	621 – 6400	7.38 ± 0.57
	500	3.98	0.9 – 8.2	29.2	435.8 – 445.0	1.27 – 11.1	949 – 8091	7.08 ± 0.46
	500	3.90	0.9 – 8.2	26.5	435.8 – 445.0	1.25 – 11.0	952 – 7832	7.09 ± 0.34
309	50	2.29	10.1 – 91.4	4.0	375.9 – 468.1	0.76 – 6.92	666 – 4983	7.17 ± 0.32
	50	2.06	9.6 – 86.9	4.0	375.9 – 468.1	0.65 – 6.00	579 – 4920	8.02 ± 0.28
323	50	2.29	10.3 – 93.5	4.0	375.9 – 468.1	0.40 – 3.68	446 – 3179	8.37 ± 0.35
	50	2.29	10.1 – 91.4	4.0	375.9 – 468.1	0.73 – 6.62	701 – 5876	8.89 ± 0.33
	50	2.06	9.6 – 86.9	4.0	375.9 – 468.1	0.63 – 5.74	613 – 4683	8.13 ± 0.27
338	50	2.12	10.1 – 92.0	4.0	375.9 – 468.1	0.49 – 4.43	507 – 3845	8.56 ± 0.28
	50	2.92	9.8 – 88.8	4.0	375.9 – 468.1	0.86 – 7.89	771 – 6734	8.40 ± 0.21
353	50	3.47	9.5 – 86.1	4.0	375.9 – 468.1	0.71 – 6.57	788 – 6225	9.57 ± 0.56
	50	3.90	5.1 – 42.4	4.0	237.5 – 283.6	0.95 – 7.95	672 – 8024	9.73 ± 0.46
	250	0.54	10.5 – 96.0	35.9	343.6 – 435.8	0.83 – 7.52	1015 – 6828	9.02 ± 0.32
	250	1.66	5.6 – 47.3	26.5	398.9 – 445.0	1.02 – 8.52	1088 – 7880	8.96 ± 0.38
	250	3.90	1.3 – 12.2	11.3	459.3 – 460.7	0.76 – 6.92	629 – 6983	9.70 ± 0.57
	500	2.99	1.3 – 12.2	35.9	422.0 – 435.8	1.16 – 10.6	1148 – 10315	9.57 ± 0.62
	500	2.92	1.4 – 12.8	35.9	422.0 – 435.8	1.19 – 10.9	1277 – 9510	9.11 ± 0.51

**Table S2.** Experimental conditions and individual rate coefficients ( $\pm 2\sigma$ ) for the OH + CHF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> reaction.

<i>T</i> / K	<i>p</i> <sub>T</sub> / Torr	<i>f</i> / 10 <sup>-2</sup>	<i>F</i> <sub>R</sub> / sccm	<i>F</i> <sub>H<sub>2</sub>O<sub>2</sub>/He</sub> / sccm	<i>F</i> <sub>He</sub> / sccm	[CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> ] / 10 <sup>15</sup> molecules cm <sup>-3</sup>	<i>k</i> '- <i>k</i> ' <sub>0</sub> / s <sup>-1</sup>	<i>k</i> <sub>OH(<i>T</i>)</sub> / 10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
263	50	1.86	6.1 – 51.0	24.4	219.0 – 265.1	0.71 – 5.90	561 – 4888	8.60 ± 0.48
	50	2.49	7.9 – 88.5	9.6	371.2 – 463.5	0.77 – 8.61	636 – 7382	8.79 ± 0.63
	250	0.74	6.6 – 55.2	27.8	214.4 – 260.5	1.54 – 12.6	1253 – 10759	8.43 ± 0.29
	250	1.86	0.8 – 9.0	46.8	232.9 – 242.1	0.48 – 5.33	247 – 4323	8.34 ± 0.52
	500	0.74	0.9 – 12.5	46.8	231.0 – 242.1	0.43 – 5.81	259 – 4897	8.23 ± 0.49
	500	3.05	0.8 – 8.4	17.0	445.0 – 454.3	0.93 – 10.0	644 – 8026	8.10 ± 0.40
268	50	3.73	6.5 – 73.9	4.0	375.9 – 468.1	0.93 – 10.9	915 – 9931	8.85 ± 0.49
	50	2.72	5.6 – 46.3	11.3	228.2 – 274.4	0.95 – 7.94	796 – 6767	8.59 ± 0.33
278	50	3.28	6.4 – 66.1	4.0	385.1 – 468.1	0.78 – 8.28	1045 – 7575	9.26 ± 0.67
	50	2.72	5.6 – 46.3	8.6	232.9 – 279.0	0.91 – 7.61	873 – 6940	9.30 ± 0.40
288	50	3.21	5.2 – 43.2	4.0	237.5 – 283.6	0.97 – 8.16	799 – 7599	9.44 ± 0.54
	50	2.72	5.6 – 46.3	4.0	237.5 – 283.6	0.88 – 7.34	747 – 6682	9.36 ± 0.31
298	50	2.66	5.6 – 46.7	4.0	237.5 – 283.6	0.83 – 6.97	783 – 6605	9.43 ± 0.20
	50	3.21	5.2 – 43.2	4.0	237.5 – 283.6	0.94 – 7.88	902 – 8029	10.2 ± 0.3
	50	3.21	5.2 – 43.2	4.0	237.5 – 283.6	0.94 – 7.88	947 – 7947	10.1 ± 0.4
	250	0.37	6.7 – 56.2	19.5	219.0 – 265.1	0.70 – 5.65	682 – 5329	9.23 ± 0.27
	250	0.37	6.7 – 56.2	18.4	223.6 – 269.8	0.69 – 5.58	614 – 5402	9.67 ± 0.33
	500	0.19	6.8 – 56.6	27.8	214.4 – 260.5	0.72 – 5.82	822 – 5752	9.80 ± 0.57
309	500	0.14	6.8 – 56.7	27.8	214.4 – 260.5	0.53 – 4.27	532 – 4272	9.86 ± 0.33
	50	2.66	5.6 – 46.7	4.0	237.5 – 283.6	0.80 – 6.72	826 – 6995	10.0 ± 0.5
	50	2.75	5.5 – 46.2	4.0	237.5 – 283.6	0.82 – 6.89	953 – 7650	10.7 ± 0.6
	323	50	2.66	5.6 – 46.7	4.0	237.5 – 283.6	0.77 – 6.43	802 – 6782
323	50	2.75	5.5 – 46.2	4.0	237.5 – 283.6	0.79 – 6.59	884 – 7103	11.1 ± 0.4
	338	50	2.66	5.6 – 46.7	4.0	237.5 – 283.6	0.73 – 6.15	832 – 7028
338	50	2.75	5.5 – 46.2	4.0	237.5 – 283.6	0.75 – 6.30	851 – 6915	10.9 ± 0.3
	353	50	2.75	5.5 – 46.2	4.0	237.5 – 283.6	0.72 – 6.03	891 – 7182
353	50	2.75	5.5 – 46.2	4.0	237.5 – 283.6	0.72 – 6.03	1005 – 7097	11.6 ± 0.5
	250	0.42	6.7 – 56.1	19.5	219.0 – 265.1	0.68 – 5.50	706 – 6205	11.2 ± 0.3
	250	0.42	6.7 – 56.1	19.5	219.0 – 265.1	0.68 – 5.50	740 – 6371	11.6 ± 0.2
	500	0.42	6.7 – 45.1	42.4	205.2 – 242.1	1.36 – 8.91	1543 – 9965	11.1 ± 0.2
	500	0.18	12.3 – 112.0	42.4	149.8 – 242.1	1.04 – 8.95	1149 – 10007	11.4 ± 0.5

**Table S3.** Experimental conditions and individual rate coefficients ( $\pm 2\sigma$ ) for the OH + CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> reaction.

$T / \text{K}$	$p_{\text{T}} / \text{Torr}$	$f / 10^{-2}$	$F_{\text{R}} / \text{sccm}$	$F_{\text{H}_2\text{O}_2/\text{He}} / \text{sccm}$	$F_{\text{He}} / \text{sccm}$	$[\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3] / 10^{15} \text{ molecules cm}^{-3}$	$k' - k'_0 / \text{s}^{-1}$	$k_{\text{OH}}(T) / 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
263	50	5.53	2.1 – 32.4	27.7	403.8 – 451.0	0.46 – 7.10	539 – 5478	$7.67 \pm 0.36$
	50	1.87	8.3 – 83.5	14.4	182.1 – 274.4	0.99 – 10.2	1023 – 8172	$7.79 \pm 0.25$
	250	2.00	0.6 – 8.1	98.6	186.7 – 195.9	0.36 – 5.06	588 – 4294	$7.89 \pm 0.60$
	250	2.00	0.6 – 8.1	14.7	265.1 – 274.4	0.36 – 5.15	532 – 4211	$8.08 \pm 0.34$
	500	1.56	0.6 – 8.3	9.8	269.8 – 279.0	0.60 – 8.30	809 – 6681	$7.85 \pm 0.36$
	500	1.87	0.6 – 8.2	19.6	260.5 – 269.8	0.69 – 9.74	977 – 8394	$8.09 \pm 0.46$
268	50	1.87	8.3 – 83.5	14.4	182.1 – 274.4	0.97 – 10.1	930 – 7997	$7.98 \pm 0.32$
	50	1.97	8.3 – 74.7	14.4	191.3 – 274.4	1.02 – 9.43	902 – 7908	$8.14 \pm 0.30$
278	50	1.97	8.3 – 66.4	4.8	209.8 – 283.6	0.99 – 8.07	935 – 6885	$8.26 \pm 0.31$
	50	2.62	4.2 – 35.8	4.8	242.1 – 283.6	0.66 – 5.77	478 – 4746	$8.32 \pm 0.49$
288	50	2.62	4.2 – 39.8	4.8	237.5 – 283.6	0.64 – 6.20	637 – 5394	$8.52 \pm 0.27$
	50	2.62	4.2 – 39.8	4.8	237.5 – 283.6	0.64 – 6.20	682 – 5296	$8.58 \pm 0.42$
298	50	2.62	4.2 – 35.8	3.8	243.0 – 284.5	0.62 – 5.38	662 – 5039	$9.14 \pm 0.68$
	50	3.07	4.2 – 38.9	3.8	238.4 – 284.5	0.73 – 6.87	736 – 6261	$8.88 \pm 0.30$
	250	0.50	3.5 – 46.0	14.4	228.2 – 274.4	0.49 – 6.45	670 – 6187	$9.45 \pm 0.33$
	250	0.50	3.5 – 14.4	14.4	228.2 – 274.4	0.49 – 6.45	777 – 6331	$9.45 \pm 0.34$
	500	2.53	0.5 – 7.8	24.6	255.9 – 265.1	0.77 – 11.1	1179 – 10045	$8.82 \pm 0.45$
	500	2.53	0.5 – 7.8	24.6	255.9 – 265.1	0.77 – 11.1	1194 – 9781	$8.74 \pm 0.49$
309	50	3.07	4.2 – 38.9	3.8	238.4 – 284.5	0.70 – 6.62	807 – 6111	$9.05 \pm 0.23$
	50	3.07	4.2 – 38.9	3.8	238.4 – 284.5	0.70 – 6.62	808 – 6159	$8.99 \pm 0.33$
323	50	3.07	4.2 – 38.9	3.8	238.4 – 284.5	0.67 – 6.34	756 – 6175	$9.66 \pm 0.26$
	50	3.07	4.2 – 38.9	3.8	238.4 – 284.5	0.67 – 6.34	843 – 6573	$10.1 \pm 0.4$
338	50	3.11	4.2 – 38.8	3.8	238.4 – 284.5	0.65 – 6.13	747 – 6436	$10.2 \pm 0.3$
	50	3.11	4.2 – 38.8	3.8	238.4 – 284.5	0.65 – 6.13	767 – 6362	$10.2 \pm 0.3$
353	50	3.11	4.2 – 35.0	4.8	242.1 – 283.6	0.62 – 5.28	890 – 6059	$11.0 \pm 0.5$
	50	3.11	4.2 – 38.8	4.8	237.5 – 283.6	0.62 – 5.87	871 – 6491	$10.7 \pm 0.4$
	250	2.53	0.5 – 7.8	14.7	265.1 – 274.4	0.33 – 4.71	683 – 5352	$10.8 \pm 0.5$
	250	2.53	0.5 – 7.8	14.7	265.1 – 274.4	0.33 – 4.71	646 – 5477	$11.0 \pm 0.5$
	500	5.38	7.8 – 81.1	105.0	299.9 – 384.9	1.17 – 12.3	1372 – 13856	$10.8 \pm 0.7$
	500	2.00	0.6 – 8.1	24.6	255.9 – 265.1	0.54 – 7.66	1050 – 8861	$10.9 \pm 0.5$
	500	2.00	0.6 – 8.1	24.6	255.9 – 265.1	0.54 – 7.66	1058 – 9222	$11.5 \pm 0.4$

**Table S4.** Summary of the reference compounds used in the relative measurements, relative rate coefficients ( $k_{\text{HFE}}/k_{\text{ref}}$ ), and rate coefficients (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for OH+Ref ( $k_{\text{ref}}$ ) and  $k_{\text{OH}}$  for the investigated HFEs (here  $k_{\text{HFE}}$ ).

HFE	Ref. compound	$k_{\text{ref}} / 10^{-13}$	$k_{\text{HFE}}/k_{\text{ref}}$	$k_{\text{HFE}} / 10^{-13}$	$k_{\text{HFE avg}} / 10^{-13}$	Reference	
CF <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	CHCl <sub>3</sub>	1.00±0.15 <sup>a</sup>	5.94±0.31	5.9±0.9	5.7±0.8	Oyaro et al. (2005)	
	CH <sub>3</sub> C(O)CH <sub>3</sub>	1.80±0.45 <sup>a</sup>	2.87±0.30	5.2±1.4			
	C <sub>2</sub> H <sub>4</sub>	85.2±12.8 <sup>b</sup>	0.053±0.005	4.5±0.8	4.9±1.3	Østerstrøm et al. (2012)	
	C <sub>2</sub> H <sub>2</sub>	8.45±0.85 <sup>c</sup>	0.63±0.05	5.3±0.4			
CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	5.54±0.27 <sup>d</sup>	1.55±0.06	8.6±0.5	8.7±0.5	Oyaro et al. (2004)	
	CHCl <sub>3</sub>	1.00±0.15 <sup>a</sup>	9.8±0.9	9.8±1.7			
CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	5.54±0.27 <sup>d</sup>	1.158±0.016	6.42±0.33	6.42±0.33	Oyaro et al. (2004)	
	C <sub>2</sub> H <sub>4</sub>	79 <sup>e</sup>	0.08±0.006	6.32±0.47		5.78±1.02	Thomsen et al. (2011)
	C <sub>2</sub> H <sub>2</sub>	7.8 <sup>e</sup>	0.67±0.04	5.23±0.31			

<sup>a</sup> Sander et al. (2003); <sup>b</sup> Calvert et al. (2000); <sup>c</sup> Sørensen et al. (2003); <sup>d</sup> Zhang et al. (1992) / Oyaro (submitted); <sup>e</sup> Atkinson et al. (2006)

**Table S5.** Comparison of the IR absorption peak for the investigated HFEs with previous values reported in the literature.

HFE	Resolution/ $\text{cm}^{-1}$	$\tilde{\nu}_{max}/ \text{cm}^{-1}$	$\sigma_{\tilde{\nu}_{max}} / 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$	Reference
$\text{CF}_3\text{CH}_2\text{OCH}_3$	1	1176	1.96	This work
	1	1176	1.72	Oyaro et al. (2005)
	0.25	1176	1.98	Østerstrøm et al. (2012)
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$	1	1131	2.12	This work
	1	1130	1.96	Oyaro et al. (2004)
$\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$	1	1212	3.11	This work
	0.25	1212	3.30	Thomsen et al. (2011)
	1	1212	2.93	Oyaro et al. (2004)

**Table S6.** Comparison of  $S_{int}$  for the investigated HFEs with previous values reported in the literature.

HFE	Range/ $\text{cm}^{-1}$	$S_{int}/ 10^{-16} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$	Reference
$\text{CF}_3\text{CH}_2\text{OCH}_3$	1525-520	$1.52 \pm 0.02$	This work
	1525-500	$1.53 \pm 0.07$	Oyaro et al. (2005)
	1600-600	$1.50 \pm 0.02$	This work
	1600-600	$1.55 \pm 0.08$	Østerstrøm et al. (2012)
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$	1520-520	$1.53 \pm 0.07$	This work
	1520-500	$1.39 \pm 0.02$	Oyaro et al. (2004)
$\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$	1500-650	$2.13 \pm 0.09$	This work
	1500-650	$2.07 \pm 0.10$	Thomsen et al. (2011)
	1525-520	$2.19 \pm 0.10$	This work
	1525-490	$1.95 \pm 0.02$	Oyaro et al. (2004)

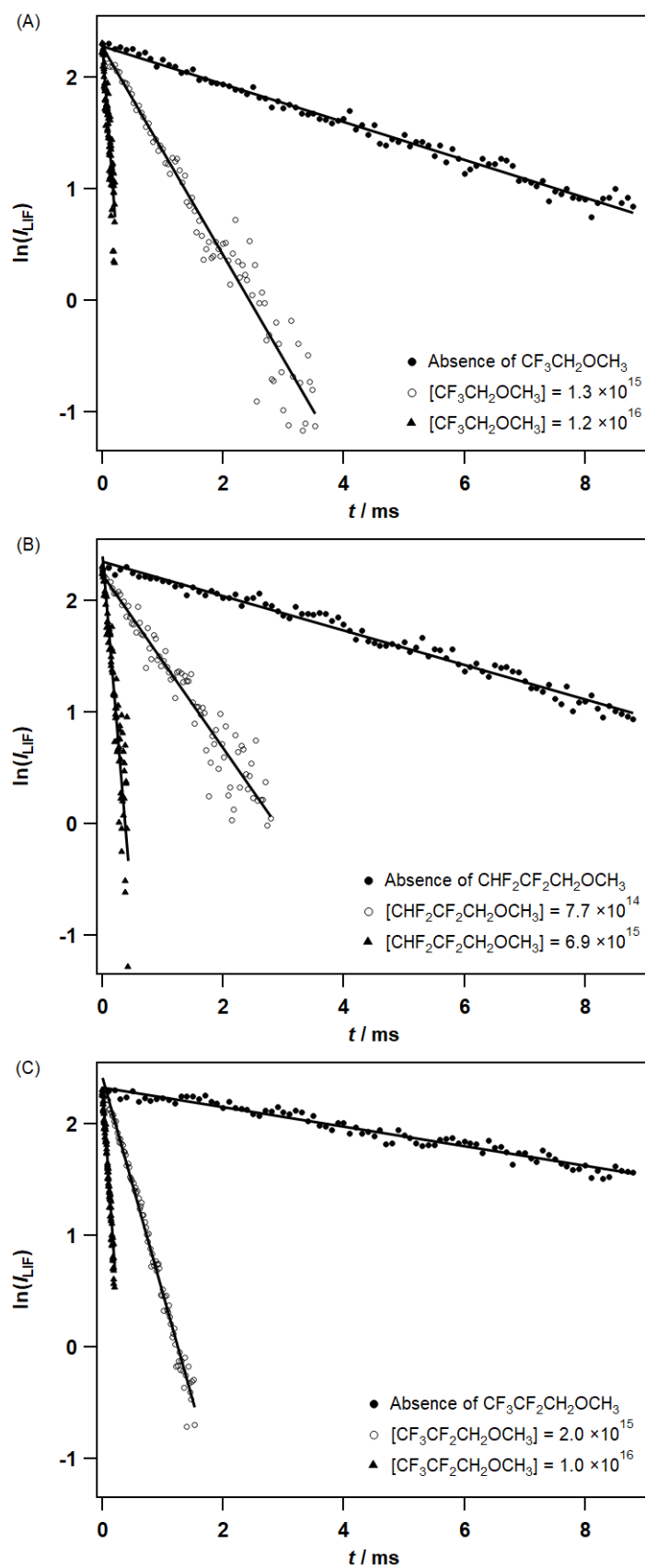
**Table S7.** Lifetimes due to OH reaction, REs, and GWPs at a time horizon of 100 years for the investigated HFEs and HFCs with the same number of C-F bonds.

Species $i$	Acronym	$\tau_{OH}$	$RE_i^{(a)}/ \text{W m}^{-2} \text{ ppbv}^{-1}$	$GWP_i(100 \text{ yrs})$	Reference
$\text{CF}_3\text{CH}_2\text{OCH}_3$	HFE-263fb2	17 days	0.031	<1	This work
$\text{CF}_3\text{CH}_2\text{CH}_3$	HFC-263fb	1.1 yrs	0.100	78	Hodnebrog et al. (2020)
$\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$	HFE-374pcf	12 days	0.030	<1	This work
$\text{CHF}_2\text{CHF}_2$	HFC-134	10.0 yrs	0.194	1330	Hodnebrog et al. (2020)
$\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$	HFE-365mcf3	13 days	0.038	<1	This work
$\text{CHF}_2\text{CF}_3$	HFC-125	30 yrs	0.234	3940	Hodnebrog et al. (2020)
$\text{CF}_3\text{CF}_2\text{CH}_3$	HFC-245cb	39.9 yrs	0.251	4790	Hodnebrog et al. (2020)

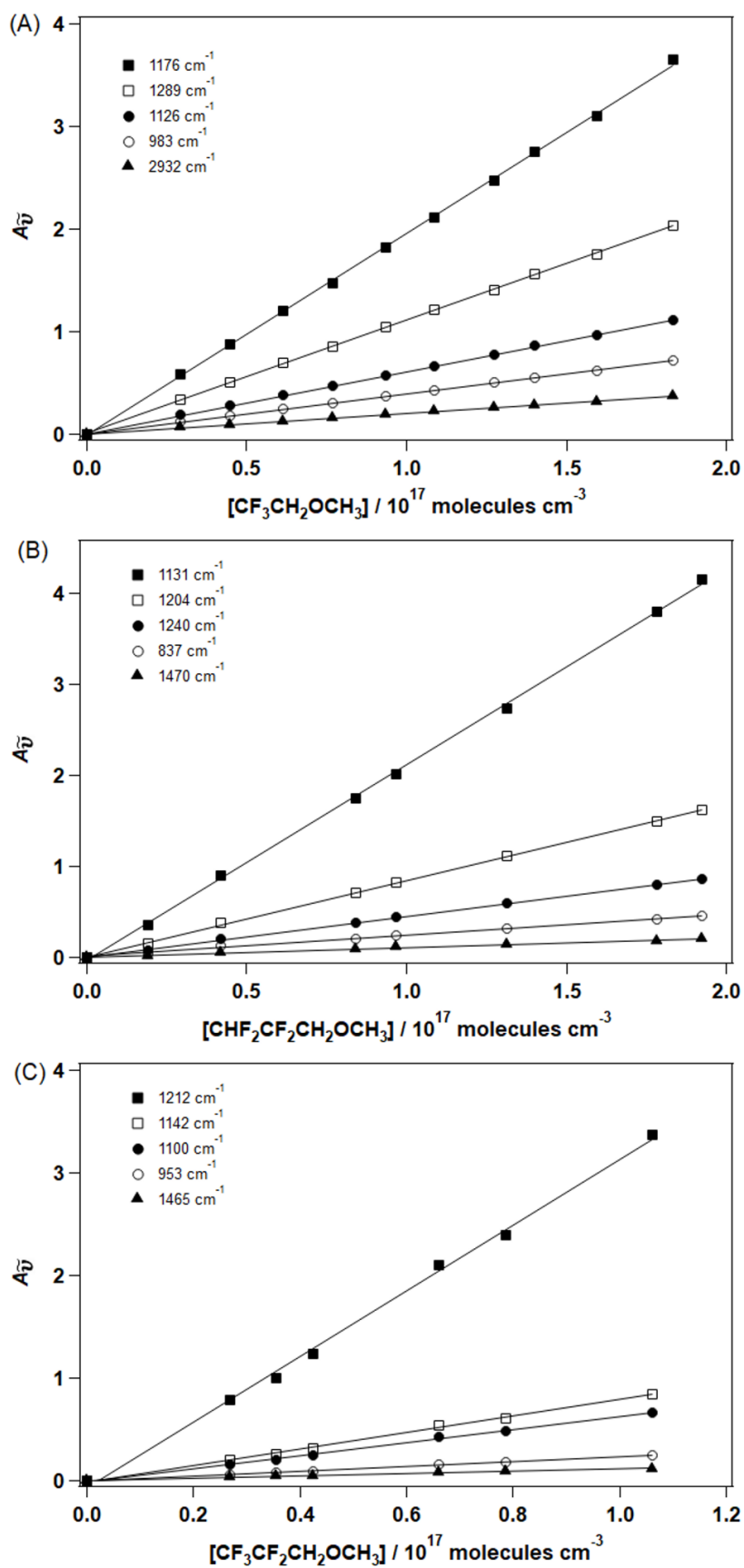
<sup>(a)</sup> Corrected with  $f_r$  factor according to Hodnebrog et al. (2020)



## SUPPLEMENTARY FIGURES



**Figure S1.** Plots of time evolution of  $I_{LIF}$  from OH radicals in the absence and presence of HFEs at 263 K and 50 Torr of He. Concentration of HFEs in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .



**Figure S2.** Plots of the Beer-Lambert's law for (A)  $\text{CF}_3\text{CH}_2\text{OCH}_3$ , (B)  $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$ , and (C)  $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCH}_3$  at several wavenumbers in the investigated IR region.

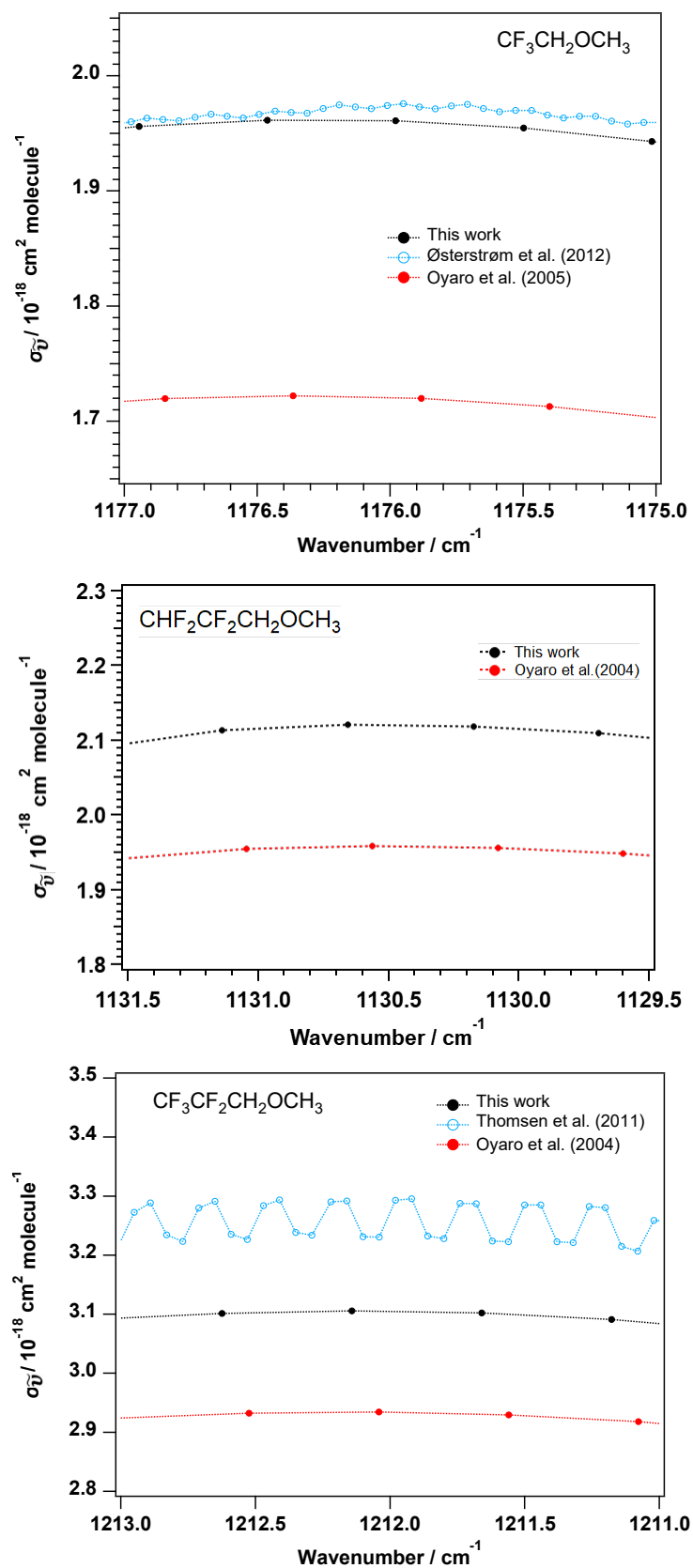


Figure S3. Zoom of the IR absorption peak for the investigated HFEs.

## REFERENCES

- Antiñolo, M., Ocaña, A. J., Aranguren, J. P., Lane, S. I., Albaladejo, J., and Jiménez, E.: *Atmospheric degradation of 2-chloroethyl vinyl ether, allyl ether and allyl ethyl ether: Kinetics with OH radicals and UV photochemistry*, Chemosphere, 181, 232-240, 2017.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: *Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species*, Atmospheric Chemistry and Physics, 6, 3625-4055, 2006.
- Blázquez, S., Antiñolo, M., Nielsen, O. J., Albaladejo, J., and Jiménez, E.: *Reaction kinetics of (CF<sub>3</sub>)<sub>2</sub>CFCN with OH radicals as a function of temperature (278–358K): a good replacement for greenhouse SF<sub>6</sub>?*, Chemical Physics Letters, 687, 297-302, 2017.
- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, Oxford, 2000.
- González, S., Jiménez, E., and Albaladejo, J.: *Assessment of the atmospheric loss processes initiated by OH radicals and sunlight, and the radiative efficiency for a series of hydrofluoroolefins, CF<sub>3</sub>(CF<sub>2</sub>)<sub>x=1,3,5</sub>CHCH<sub>2</sub>*, Chemosphere, 151, 45-54, 2016.
- González, S., Jiménez, E., Ballesteros, B., Martínez, E., and Albaladejo, J.: *Hydroxyl radical reaction rate coefficients as a function of temperature and IR absorption cross sections for CF<sub>3</sub>CH=CH<sub>2</sub> (HFO-1243zf), potential replacement of CF<sub>3</sub>CH<sub>2</sub>F (HFC-134a)*, Environmental Science and Pollution Research, 22, 4793-4805, 2015.
- Hodnebrog, Ø., Etmann, M., Fuglestedt, J. S., Marston, G., Myhre, G., Nielsen, C. J., Shine, K. P., and Wallington, T. J.: *Global warming potentials and radiative efficiencies of halocarbons and related compounds: A comprehensive review*, Rev. Geophys., 51, 300-378, 2013.
- Hodnebrog, Ø., Aamaas, B., Fuglestedt, J. S., Marston, G., Myhre, G., Nielsen, C. J., Sandstad, M., Shine, K. P., and Wallington, T. J.: *Updated Global Warming Potentials and Radiative Efficiencies of Halocarbons and Other Weak Atmospheric Absorbers*, Reviews of Geophysics, 58, e2019RG000691, 2020.
- Jiménez, E., González, S., Cazaunau, M., Chen, H., Ballesteros, B., Daële, V., Albaladejo, J., and Mellouki, A.: *Atmospheric Degradation Initiated by OH Radicals of the Potential Foam Expansion Agent, CF<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub> (HFC-1447fz): Kinetics and Formation of Gaseous Products and Secondary Organic Aerosols*, Environmental Science & Technology, 50, 1234-1242, 2016.
- Østerstrøm, F. F., Nielsen, O. J., Sulbaek Andersen, M. P., and Wallington, T. J.: *Atmospheric chemistry of CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>: Reaction with chlorine atoms and OH radicals, kinetics, degradation mechanism and global warming potential*, Chemical Physics Letters, 524, 32-37, 2012.
- Oyaro, N., Sellevåg, S. R., and Nielsen, C. J.: *Study of the OH and Cl-Initiated Oxidation, IR Absorption Cross-Section, Radiative Forcing, and Global Warming Potential of Four C4-Hydrofluoroethers*, Environmental Science & Technology, 38, 5567-5576, 2004.
- Oyaro, N., Sellevåg, S. R., and Nielsen, C. J.: *Atmospheric Chemistry of Hydrofluoroethers: Reaction of a Series of Hydrofluoroethers with OH Radicals and Cl Atoms, Atmospheric Lifetimes, and Global Warming Potentials*, The Journal of Physical Chemistry A, 109, 337-346, 2005.
- Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 14*, National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 2003.
- Shine, K. P. and Myhre, G.: *The Spectral Nature of Stratospheric Temperature Adjustment and its Application to Halocarbon Radiative Forcing*, Journal of Advances in Modeling Earth Systems, 12, e2019MS001951, 2020.
- Sørensen, M., Kaiser, E. W., Hurley, M. D., Wallington, T. J., and Nielsen, O. J.: *Kinetics of the reaction of OH radicals with acetylene in 25–8000 torr of air at 296 K*, International Journal of Chemical Kinetics, 35, 191-197, 2003.
- Thomsen, D. L., Andersen, V. F., Nielsen, O. J., and Wallington, T. J.: *Atmospheric chemistry of C<sub>2</sub>F<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub> (HFE-365mcf)*, Physical Chemistry Chemical Physics, 13, 2758-2764, 2011.
- Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: *Rate constants for reactions of the hydroxyl radical with several partially fluorinated ethers*, The Journal of Physical Chemistry, 96, 9301-9304, 1992.