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Climate Metrics for C1−C4 Hydrofluorocarbons (HFCs)

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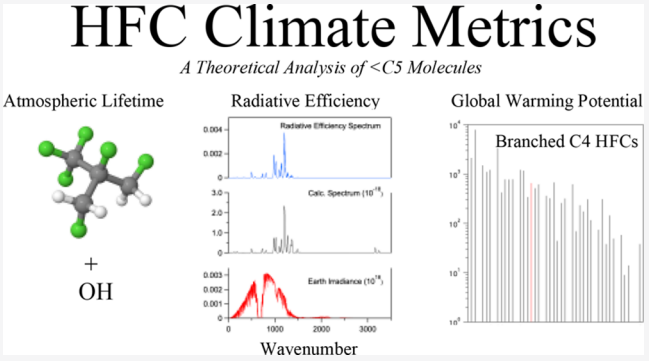
ABSTRACT: Hydrofluorocarbons (HFCs) are potent greenhouse gases that are potential substitutes for ozone depleting substances. The Kigali amendment lists 17 HFCs that are currently in commercial use to be regulated under the Montreal Protocol. Future commercial applications may explore the use of other HFCs, most of which currently lack an evaluation of their climate metrics. In this work, atmospheric lifetimes, radiative efficiencies (REs), global warming potentials (GWPs), and global temperature change potentials (GTPs) for all saturated HFCs with fewer than 5 carbon atoms are estimated to help guide future usage and policy decisions. Atmospheric lifetimes were estimated using a structure activity relationship (SAR) for OH radical reactivity and estimated $O(^1D)$ reactivity. Radiative metrics were obtained using theoretically calculated infrared absorption spectra that were presented in a previous work. Calculations for some additional HFCs not included in the previous work were performed in this work. The HFCs display unique infrared spectra with strong absorption in the Earth's atmospheric infrared window region, primarily due to the C−F stretching vibration. Results from this study show that the HFC global atmospheric lifetimes and REs are dependent upon their H atom content and molecular structure. Therefore, the HFC radiative metric evaluation requires a case-by-case evaluation. A thorough experimental evaluation of a targeted HFC's atmospheric lifetime and climate metrics is always highly recommended. However, in cases where it is experimentally difficult to separate isomers, the new results from this study should help guide the experiments, as well as provide relevant climate metrics with uncertainties and policy relevant data.



INTRODUCTION

Hydrofluorocarbons (HFCs) are, in general, potent greenhouse gases due to their strong infrared absorption in the Earth's atmospheric "window" region. HFCs are a current environmental concern because of their potential use as replacements for ozone depleting substances. Seventeen HFCs that are in commercial use today have been included in the Kigali amendment for regulation and phase-down under the Montreal Protocol (see Table 1). The atmospheric lifetimes and climate metrics (radiative efficiency (RE), global warming potential (GWP), and global temperature change potential (GTP)) for these HFCs have been defined based on detailed experimental studies of their OH reactivity and infrared absorption, as summarized in the World Meteorological Organization (WMO) ozone assessment report.[1] In the future, commercial applications may wish to explore the use of other HFCs that are currently not included in the Montreal Protocol, nearly all of which lack a rigorous evaluation of their atmospheric lifetime and climate metrics.

In this work, estimates of atmospheric lifetimes, REs, GWPs, and GTPs for all HFCs with fewer than 5 carbon atoms are reported. Atmospheric lifetimes were estimated using a structure activity relationship (SAR) for OH radical reactivity and estimated $O(^1D)$ reactivity. Photolytic loss, which is expected to be primarily an upper-atmosphere loss process for HFCs, is negligible and was not evaluated as part of this work. Radiative metrics were determined using theoretically calculated infrared absorption spectra presented in the work of Bera et al.[2] and Kokkila et al.[3] and supplemented in this work using the same theoretical methods. The calculated infrared spectra display strong absorption in the Earth's atmospheric infrared (IR) window region, primarily due to the C−F stretching vibrational mode. The estimated lifetimes and radiative metrics for compounds with parameters listed in the WMO report, which are primarily based on experimental measurements, are used to validate our methods and provide a basis to estimate parameter uncertainties. The results from this study are intended to provide policy-relevant climate metrics for lightweight HFCs that are currently lacking quantitative experimental studies. This study does not, however, replace

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Table 1. Summary of C1−C2 Hydrofluorocarbon (HFC) Atmospheric Lifetimes and Climate Metrics[a]

Formula	Abbrev.	CAS RN	Total Lifetime (years)	Tropospheric OH Lifetime (years)	Stratospheric Lifetime (years)	RE	GWP 20	GWP 100	GTP 20	GTP 50	GTP 100
C1 Molecules											
CHF_3	HFC-23	75-46-7	228	243	4420	0.18	11085	12690	11825	13340	13150
CH_2F_2	HFC-32	75-10-5	5.4	5.5	124	0.11	2530	705	1440	154	98
CH_3F	HFC-41	593-53-3	2.8	2.9	65	0.02	430	116	177	21	16
C2 Molecules											
CHF_2-CF_3	HFC-125	354-33-6	30	32	595	0.23	6280	3450	6040	3350	1180
CHF_2-CHF_2	HFC-134	359-35-3	10	10.5	240	0.19	3625	1135	2725	440	164
CH_2F-CF_3	HFC-134a	811-97-2	14	14.1	267	0.16	3810	1360	3170	770	215
CH_2F-CHF_2	HFC-143	430-66-0	3.6	3.70	100	0.13	1250	340	580	64	48
CH_3-CF_3	HFC-143a	420-46-2	51	57	612	0.16	7050	5080	7110	5390	2830
CH_2F-CH_2F	HFC-152	624-72-6	172 days	172 days	25	0.04	64	17	20	3.0	2.4
CH_3-CHF_2	HFC-152a	75-37-6	1.6	1.55	39	0.10	545	148	190	26	21
CH_3-CH_2F	HFC-161	353-36-6	80 days	80 days	25	0.02	20	6	6	<1	<1

[a]The gray shaded entries were taken from WMO (2018). The results from the present work for these HFCs are given in the Supporting Information datasheets. All other entries are from this work. The values reported in this work were obtained using methods consistent with the methods used to derive the WMO (2018) lifetimes and climate metrics: Radiative efficiency (RE) in units of W m^{-2} ppb^{-1}; Global Warming Potential (GWP) and time-horizon; and Global Temperature Potential (GTP) and time-horizon.

the need for detailed experimental studies of specific targeted compounds prior to their commercial use.

METHODOLOGY

Atmospheric Lifetimes. The global HFC atmospheric lifetime (τ_{atm}) is defined as

$$\frac{1}{\tau_{atm}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O(^1D)}}$$

where τ_{OH} and $\tau_{O(1D)}$ are the global lifetimes with respect to OH and $O(^1D)$ reactive loss, respectively. τ_{atm} can also be expressed in terms of its troposphere (τ_{Trop}), stratosphere (τ_{Strat}), and mesosphere (τ_{Meso}) lifetimes

$$\frac{1}{\tau_{atm}} = \frac{1}{\tau_{Trop}} + \frac{1}{\tau_{Strat}} + \frac{1}{\tau_{Meso}}$$

where, for example

$$\frac{1}{\tau_{Strat}} = \frac{1}{\tau_{Strat}^{OH}} + \frac{1}{\tau_{Strat}^{O(^1D)}}$$

For the HFCs considered in this study, mesospheric loss is expected to be negligible and not considered further. In this work, τ_{Trop}^{OH} was estimated using the CH_3CCl_3 (MCF) relative lifetime method[4] where

$$\tau_{Trop}^{OH} = \tau_{OH}^{HFC} = \frac{k_{MCF}(272\ K)}{k_{HFC}(272\ K)}\tau_{OH}^{MCF}$$

with the MCF recommended OH reaction rate coefficient, $k_{MCF}(272\ K) = 6.14 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1},[5] and τ_{OH}^{MCF} is the recommended tropospheric lifetime of MCF, 6.1 years,[4] due to reaction with the OH radical.

In the absence of experimentally determined OH reaction rate coefficients, the structure activity relationship (SAR) developed by DeMore[6] was used to estimate OH reaction rate coefficients. For the determination of $k_{HFC}(272\ K)$, the reaction rate coefficient E/R was estimated based on the trend in Arrhenius parameters, $k(T) = A\exp(-E/RT)$, for the HFCs recommended in Burkholder et al.;[5] $E/R = \exp(1.9686 - 0.15697\ k(298\ K))$ K. On the basis of a comparison with recommended rate coefficient data, the uncertainty in the SAR room temperature rate coefficients is estimated to be better than 30%, as shown in Figure 1. The uncertainty in $k(272\ K)$ will, most likely, be greater due to the uncertainty in the assumed E/R value. We estimate a 50% uncertainty in $k(272\ K)$ for all compounds in this study.

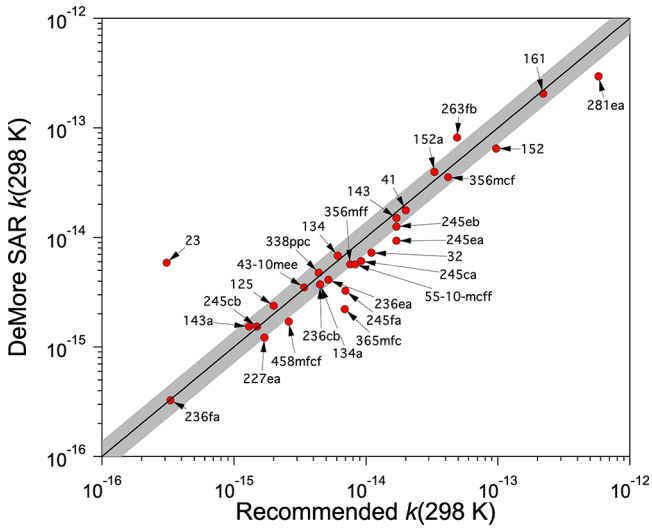

Figure 1. Correlation between the 298 K OH + hydrofluorocarbon (HFC) reaction rate coefficients, $k(298\ K)$, calculated using the structure activity relationship (SAR) from DeMore[6] and the recommended values from Burkholder et al.[5] (28 HFCs in total). The HFCs are labeled on the graph. The line is the 1:1 relationship. The edges of the gray shaded region represent the ±30% range around the 1:1 line.

τ_{Strat} for the HFCs was determined from a combination of OH and $O(^1D)$ reactive loss. We estimated stratospheric OH loss lifetimes, τ_{Strat}^{OH}, following the methodology used in WMO-2014[1] and our previous study of HCFCs climate metrics.[7] $O(^1D)$ rate coefficients were estimated using the reactivity trends reported in Baasandorj et al.[8] In most cases, the stratospheric loss via the OH reaction accounts for approximately ≤5% of the total OH loss process. The $O(^1D)$ reaction represents only a minor contributor to the global loss of the HFCs, <2%. A minimum stratospheric lifetime of 25

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Table 2. Summary of C3 Hydrofluorocarbon (HFC) Atmospheric Lifetimes and Climate Metrics[a]

Formula	Abbrev.	CAS RN	Total Lifetime (years)	Tropospheric OH Lifetime (years)	Stratospheric Lifetime (years)	RE	GWP 20	GWP 100	GTP 20	GTP 50	GTP 100
CHF_2-CF_2-CF_3	HFC-227ca	2252-84-8	30	32	640	0.27	5260	2865	5070	2795	975
CF_3-CHF-CF_3	HFC-227ea	431-89-0	36	37.5	673	0.26	5250	3140	5140	3180	1260
CHF_2-CF_2-CHF_2	HFC-236ca	680-00-2	11.4	11.9	268	0.304	4259	1399	3327	622	205
CH_2F-CF_2-CF_3	HFC-236cb	677-56-5	13.4	14	305	0.23	3540	1235	2915	670	192
CHF_2-CHF-CF_3	HFC-236ea	431-63-0	11.4	11.9	270	0.30	4190	1370	3290	620	202
CF_3-CH_2-CF_3	HFC-236fa	690-39-1	213	253	1350	0.24	6785	7680	7230	8090	7870
CH_2F-CF_2-CHF_2	HFC-245ca	679-86-7	6.6	6.9	165	0.24	2530	720	1600	180	102
CH_3-CF_2-CF_3	HFC-245cb	1814-88-6	39.9	43	550	0.24	6340	4000	6280	4150	1800
CHF_2-CHF-CHF_2	HFC-245ea	24270-66-4	3.2	3.3	95	0.16	860	233	375	44	32
CH_2F-CHF-CF_3	HFC-245eb	431-31-2	3.2	3.3	90	0.20	1070	290	460	54	40
CHF_2-CH_2-CF_3	HFC-245fa	460-73-1	7.9	8.2	149	0.24	2980	880	2040	260	124
CH_2F-CF_2-CH_2F	HFC-254ca	813-75-2	2.56	2.65	74.5	0.147	734	200	292	36	28
CH_3-CF_2-CHF_2	HFC-254cb	40723-63-5	10.8	11.4	228	0.203	3603	1164	2772	490	169
CH_2F-CHF-CHF_2	HFC-254ea	24270-68-6	1.94	2.01	59	0.173	655	178	239	31	25
CH_3-CHF-CF_3	HFC-254eb	421-48-7	2.25	2.33	67	0.178	782	213	298	38	29
CHF_2-CH_2-CHF_2	HFC-254fa	66794-30-7	3.99	4.14	107	0.236	1824	500	887	97	69
CH_2F-CH_2-CF_3	HFC-254fb	460-36-6	1.38	1.43	44	0.155	419	114	142	20	16
CH_3-CF_2-CH_2F	HFC-263ca	811-94-9	3.67	3.81	98	0.141	1187	324	554	62	45
CH_2F-CHF-CH_2F	HFC-263ea	66794-36-3	0.53	0.55	25	0.071	87	24	27	4	3
CH_3-CHF-CHF_2	HFC-263eb	66794-35-2	1.09	1.12	36	0.118	298	81	97	14	11
CH_2F-CH_2-CHF_2	HFC-263fa	24270-67-5	1.07	1.10	35	0.126	311	85	102	14	12
CH_3-CH_2-CF_3	HFC-263fb	421-07-8	1.1	1.16	40	0.10	250	68	83	12	9.5
CH_3-CF_2-CH_3	HFC-272ca	420-45-1	9	9.7	185	0.07	1580	480	1140	163	69
CH_3-CHF-CH_2F	HFC-272ea	62126-90-3	0.38	0.38	25	0.055	58	16	18	3	2
CH_2F-CH_2-CH_2F	HFC-272fa	462-39-5	0.19	0.19	25	0.037	20	5	6	1	1
CH_3-CH_2-CHF_2	HFC-272fb	430-61-5	0.71	0.73	25	0.077	153	42	48	7	6
CH_3-CHF-CH_3	HFC-281ea	420-26-8	27 days	27 days	25	0.019	11	3	3	0.50	0.40
CH_3-CH_2-CH_2F	HFC-281fa	460-13-9	0.13	0.13	25	0.016	8	2	2	0.35	0.29

[a]The gray shaded entries were taken from WMO (2018). The results from the present work for these HFCs are given in the Supporting Information datasheets. All other entries are from this work. The values reported in this work were obtained using methods consistent with the methods used to derive the WMO (2018) lifetimes and climate metrics: Radiative efficiency (RE) in units of W m^{-2} ppb^{-1}; Global Warming Potential (GWP) and time-horizon; and Global Temperature Potential (GTP) and time-horizon.

years was applied to account for transport limited stratospheric lifetimes.

Quantum Chemistry Calculations. The theoretical methods used to calculate HFC infrared absorption spectra are taken from Bera et al.[2] and Kokkila et al.[3] Calculations were performed using second-order Møller−Plesset perturbation theory (MP2) using the frozen-core approximation together with a double-ζ plus polarization one-particle basis set that includes diffuse functions on all atoms, including H, and is denoted DZP++.[9−12] The present study includes branched C4 HFCs, which were not part of the Kokkila et al.[3] study. The calculated spectra used in this work are for the lowest-energy structure obtained after very tight geometry optimizations and have been computed using the double harmonic approximation, following Kokkila et al.

The level of theory was evaluated based on comparison with available experimental HFC infrared spectra. Although the properties of each HFC may vary, as stated by Kokkila et al., on the basis of comparisons to experiment the theoretically computed infrared spectra band strengths are estimated to be between 5% and ∼20% larger than experiment. There has not been a systematic study comparing the C−F stretching harmonic frequencies computed at the MP2/DZP++ level of theory with experimental fundamental vibrational frequencies, but there are at least two relevant studies that give us an idea of the uncertainty of the band centers. Simandiras et al.[13] report MP2/DZP harmonic frequencies for fluoroethane and find that the C−F stretching harmonic frequency is computed to be about 21 cm^{-1} higher than experiment, which amounts to an error of about 2.4%. In this case, the majority of that error is probably the neglect of an anharmonic correction for the C−F stretch. Second, Breidung et al.,[14] using the MP2/DZP level of theory, compute the symmetric and antisymmetric C−F stretches of difluorethyne to be 22 cm^{-1} too low and 8 cm^{-1} too high compared to experimental fundamental vibrational frequencies, respectively. These amount to errors of −2.8% and 0.6%, respectively. Hence, for the majority of the HFCs included in this study, we would expect the band centers to be within ±3% or better. All of the new calculations have been run with the Q-Chem 5 quantum chemistry package.[15]

Climate Metrics. Radiative efficiencies (REs) were calculated using the 298 K calculated infrared absorption spectra and the parameterization of the Earth's irradiance given in Hodnebrog et al.[16] The calculated spectra were broadened using a Gaussian function with a fwhm (full width at half-maximum) of 20 cm^{-1} to provide a more realistic representation of the spectrum band widths and overlap with Earth's irradiance profile. Note that the calculated infrared spectra include vibrational bands below 500 cm^{-1}, which is usually the lower limit for experimental infrared absorption spectra measurements. The contribution of vibrational bands in this region is, however, usually minor, i.e., <1%.

Atmospheric lifetime-adjusted REs were calculated using the parameterization developed in Hodnebrog et al.[16] for compounds dominated by tropospheric OH loss with a "CFC-11-like" emission distribution. A +10% correction was

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Table 3. Summary of Linear-C4 Hydrofluorocarbon (HFC) Atmospheric Lifetimes and Climate Metrics[a]

Formula	Abbrev.	CAS RN	Total Lifetime (years)	Tropospheric OH Lifetime (years)	Stratospheric Lifetime (years)	RE	GWP 20	GWP 100	GTP 20	GTP 50	GTP 100
CHF_2-CF_2-CF_2-CF_3	HFC-329p	375-17-7	32	34	675	0.31	4720	2630	4565	2595	935
CF_3-CHF-CF_2-CF_3	HFC-329me	680-17-1	48.2	50.9	885	0.328	5515	3862	5524	4067	2047
CH_2F-CF_2-CF_2-CF_3	HFC-338q	662-35-1	14.6	15.3	325	0.276	3369	1229	2831	728	197
CHF_2-CHF-CF_2-CF_3	HFC-338mce	119450-58-7	9.27	9.66	228	0.305	2795	860	2034	300	122
CHF_2-CF_2-CHF-CF_3	HFC-338mec	35230-11-6	11.7	12.2	274	0.322	3458	1149	2728	530	169
CHF_2-CF_2-CF_2-CHF_2	HFC-338pcc	377-36-6	13.5	14.0	360	0.324	3407	1119	2662	498	164
CF_3-CH_2-CF_2-CF_3	HFC-338mf	2924-29-0	184	214	1289	0.307	6514	7214	6894	7562	7115
CF_3-CHF-CHF-CF_3	HFC-338mee	75995-72-1	11.4	11.9	269	0.338	3571	1175	2795	526	172
CH_3-CF_2-CF_2-CF_3	HFC-347mcc	662-00-0	36.8	39.5	529	0.253	4789	2902	4685	2938	1191
CH_2F-CHF-CF_2-CF_3	HFC-347mce	75995-85-6	3.35	3.47	95	0.236	969	264	432	49	37
CH_2F-CF_2-CHF-CF_3	HFC-347mec	53005-35-9	4.22	4.37	116	0.264	1357	372	679	73	52
CH_2F-CF_2-CF_2-CHF_2	HFC-347pcc	119450-61-2	8.70	9.08	205	0.287	2759	834	1958	271	118
CHF_2-CH_2-CF_2-CF_3	HFC-347mcf	161791-36-2	8.64	9.02	204	0.326	3115	940	2205	303	133
CHF_2-CHF-CHF-CF_3	HFC-347mee	151868-61-0	5.00	5.20	133	0.298	1795	497	981	104	69
CHF_2-CHF-CF_2-CHF_2	HFC-347pce	119450-64-5	6.43	6.70	162	0.288	2176	620	1351	151	87
CHF_2-CF_2-CH_2-CF_3	HFC-347mfc	119450-65-6	14.6	15.4	300	0.308	4118	1502	3459	888	241
CF_3-CH_2-CHF-CF_3	HFC-347mef	86884-16-4	8.53	8.90	202	0.318	3010	906	2119	288	128
CH_3-CHF-CF_2-CF_3	HFC-356mce	161791-32-8	2.25	2.33	67	0.204	626	170	239	30	24
CH_3-CF_2-CHF-CF_3	HFC-356mec	76523-97-2	13.9	14.6	268	0.251	3623	1290	3001	720	201
CH_3-CF_2-CF_2-CHF_2	HFC-356pcc	119450-66-7	10.8	11.4	228	0.262	3254	1051	2503	442	152
CH_2F-CH_2-CF_2-CF_3	HFC-356mcf	161791-33-9	1.2	1.26	40	0.214	404	110	137	19	15
CH_2F-CHF-CHF-CF_3	HFC-356mee	119450-67-8	2.21	2.28	66	0.220	661	180	251	32	25
CH_2F-CHF-CF_2-CHF_2	HFC-356pce	119450-68-9	2.87	2.98	82	0.220	859	234	358	43	32
CH_2F-CF_2-CH_2-CF_3	HFC-356mfc	76546-55-9	4.84	5.03	125	0.249	1611	445	866	92	62
CH_2F-CF_2-CHF-CHF_2	HFC-356pec	114810-03-6	2.83	2.93	81	0.228	878	239	364	44	33
CHF_2-CH_2-CHF-CF_3	HFC-356mef	158421-88-6	2.71	2.81	78	0.260	961	262	391	47	36
CHF_2-CHF-CH_2-CF_3	HFC-356mfe	76523-98-3	3.05	3.17	86	0.263	1093	298	468	55	41
CHF_2-CH_2-CF_2-CHF_2	HFC-356pcf	119450-69-0	5.43	5.66	137	0.270	1946	543	1111	119	76
CHF_2-CHF-CHF-CHF_2	HFC-356pee	392-45-0	3.17	3.29	89	0.251	1081	295	470	55	41
CF_3-CH_2-CH_2-CF_3	HFC-356mff	407-59-0	8.5	8.9	190	0.300	3383	1045	2474	371	149
CH_2F-CF_2-CF_2-CH_2F	HFC-356qcc	114810-02-5	7.03	7.34	166	0.239	2154	622	1395	163	87
CH_3-CH_2-CF_2-CF_3	HFC-365mcf	37826-35-0	1.64	1.69	50	0.193	483	131	169	23	18
CH_3-CHF-CHF-CF_3	HFC-365mee	161791-22-6	1.09	1.12	36	0.174	289	79	94	13	11
CH_3-CHF-CF_2-CHF_2	HFC-365pce	158421-89-7	4.35	4.52	112	0.203	1333	366	677	73	51
CH_3-CF_2-CHF-CHF_2	HFC-365pec	119450-71-4	5.44	5.67	132	0.211	1710	477	976	104	67
CH_3-CF_2-CF_2-CH_2F	HFC-365qcc	119450-72-5	10.1	10.6	205	0.222	2952	932	2216	360	134
CH_3-CF_2-CH_2-CF_3	HFC-365mfc	406-58-6	10.9	11.4	215	0.215	3005	972	2315	410	141
CH_2F-CH_2-CHF-CF_3	HFC-365mef	161791-23-7	1.07	1.10	35	0.180	294	80	96	14	11
CH_2F-CH_2-CF_2-CHF_2	HFC-365pcf	161791-25-9	1.26	1.30	40	0.180	347	94	116	16	13
CH_2F-CHF-CH_2-CF_3	HFC-365mfe	161791-24-8	0.84	0.87	28	0.167	214	58	68	10	8
CH_2F-CHF-CHF-CHF_2	HFC-365qee	157016-17-6	1.96	2.03	59	0.178	535	146	196	26	20
CH_2F-CF_2-CH_2-CHF_2	HFC-365pfc	119450-76-9	3.28	3.40	89	0.208	1041	284	460	53	39
CH_2F-CF_2-CHF-CH_2F	HFC-365qce	119450-75-8	2.07	2.15	62	0.166	526	143	196	25	20
CHF_2-CH_2-CH_2-CF_3	HFC-365mff	161879-85-2	3.32	3.44	90	0.250	1263	344	561	64	48
CHF_2-CH_2-CHF-CHF_2	HFC-365pef	119450-77-0	2.14	2.22	63	0.214	699	190	262	34	26
CF_3-CHF-CH_2-CH_3	HFC-374mef	161791-15-7	0.63	0.65	25	0.135	148	40	46	7	6
CF_3-CH_2-CHF-CH_3	HFC-374mfe	86884-13-1	0.49	0.50	25	0.124	106	29	32	5	4
CF_3-CH_2-CH_2-CH_2F	HFC-374mff	83234-21-3	0.21	0.21	25	0.078	29	8	9	1	1
CHF_2-CF_2-CH_2-CH_3	HFC-374pcf	143969-51-1	0.79	0.81	27	0.136	187	51	59	9	7
CHF_2-CHF-CHF-CH_3	HFC-374pee	161791-16-8	0.91	0.94	30	0.125	198	54	63	9	7
CHF_2-CHF-CH_2-CH_2F	HFC-374pef	161791-17-9	0.86	0.89	29	0.137	205	56	65	9	8
CHF_2-CH_2-CF_2-CH_3	HFC-374pfc	625-09-2	3.00	3.12	82	0.178	926	252	394	46	35
CHF_2-CH_2-CHF-CH_2F	HFC-374pfe	161791-18-0	0.75	0.77	26	0.126	164	45	51	8	6
CH_2F-CF_2-CHF-CH_3	HFC-374qce	161791-20-4	1.54	1.59	47	0.141	377	103	130	18	14
CH_2F-CHF-CF_2-CH_3	HFC-374qec	161791-19-1	2.29	2.37	66	0.151	601	163	230	29	23
CH_2F-CF_2-CH_2-CH_2F	HFC-374qcf	161791-21-5	1.07	1.11	35	0.133	248	68	81	12	9
CH_2F-CHF-CHF-CH_2F	HFC-374qee	119382-47-7	1.20	1.24	38	0.121	252	69	84	12	9
CH_3-CF_2-CF_2-CH_3	HFC-374scc	421-74-9	17.6	18.8	268	0.212	4410	1759	3865	1237	321
CHF_2-CH_2-CH_2-CHF_2	HFC-374pff	161879-84-1	1.38	1.43	43	0.179	432	117	146	20	16
CH_3-CH_2-CH_2-CF_3	HFC-383m	460-34-4	0.19	0.19	25	0.064	25	7	7	1	1
CHF_2-CHF-CH_2-CH_3	HFC-383pe	66675-41-0	0.48	0.49	25	0.090	88	24	27	4	3
CHF_2-CH_2-CHF-CH_3	HFC-383pfe	66675-42-1	0.45	0.46	25	0.095	86	23	26	4	3
CHF_2-CH_2-CH_2-CH_2F	HFC-383pff	66587-70-0	0.20	0.20	25	0.099	40	11	12	2	1
CH_2F-CF_2-CH_2-CH_3	HFC-383qcf	66587-71-1	1.22	1.26	38	0.110	270	73	89	13	10
CH_2F-CHF-CHF-CH_3	HFC-383qee	66587-72-2	0.37	0.37	25	0.066	48	13	15	2	2
CH_2F-CHF-CH_2-CH_2F	HFC-383qef	66587-73-3	0.49	0.50	25	0.071	71	19	22	3	3
CH_2F-CH_2-CF_2-CH_3	HFC-383qfc	66587-74-4	1.10	1.14	35	0.108	241	66	79	11	9
CH_3-CF_2-CHF-CH_3	HFC-383sce	66587-75-5	1.19	1.23	38	0.118	283	77	94	13	11
CH_3-CH_2-CH_2-CHF_2	HFC-392pff	2358-38-5	0.17	0.17	25	0.037	15	4	4	1	1
CH_3-CH_2-CHF-CH_2F	HFC-392qef	686-65-7	0.28	0.28	25	0.040	26	7	8	1	1
CH_3-CHF-CH_2-CH_2F	HFC-392qfe	691-42-9	0.31	0.32	25	0.044	33	9	10	1	1
CH_2F-CH_2-CH_2-CH_2F	HFC-392qff	372-90-7	0.11	0.11	25	0.026	7	2	2	0	0
CH_3-CH_2-CF_2-CH_3	HFC-392scf	353-81-1	0.78	0.80	26	0.080	150	41	47	7	6
CH_3-CHF-CHF-CH_3	HFC-392see	666-21-7	0.28	0.28	25	0.045	30	8	9	1	1
CH_3-CH_2-CH_2-CH_2F	HFC-3-10-1q	2366-52-1	0.08	0.08	25	0.011	3	1	1	0	0
CH_3-CH_2-CHF-CH_3	HFC-3-10-1se	359-01-3	0.10	0.10	25	0.014	4	1	1	0	0

[a]The gray shaded entries were taken from WMO (2018). The results from the present work for these HFCs are given in the Supporting Information datasheets. All other entries are from this work. The values reported in this work were obtained using methods consistent with the methods used to derive the WMO (2018) lifetimes and climate metrics: Radiative efficiency (RE) in units of W m^{-2} ppb^{-1}; Global Warming Potential (GWP) and time-horizon; and Global Temperature Potential (GTP) and time-horizon.

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Table 4. Summary of Branched-C4 Hydrofluorocarbon (HFC) Atmospheric Lifetimes and Climate Metrics[a]

Formula	Abbrev.	CAS RN	Total Lifetime (years)	Tropospheric OH Lifetime (years)	Stratospheric Lifetime (years)	RE	GWP 20	GWP 100	GTP 20	GTP 50	GTP 100
CHF_2-$CF(CF_3)$-CF_3	HFC-*b*-329my	59571-40-3	23.7	24.8	523	0.325	4514	2124	4179	1838	527
CF_3-$CH(CF_3)$-CF_3	HFC-*b*-329mz	382-24-1	589	740	2879	0.307	6213	7905	6663	8079	8991
CHF_2-$CH(CF_3)$-CF_3	HFC-*b*-338mz	382-20-7	15.19	15.92	334	0.324	4035	1498	3421	921	246
CHF_2-$CF(CF_3)$-CHF_2	HFC-*b*-338py	65781-21-7	11.35	11.86	267.8	0.320	3372	1108	2634	493	162
CH_2F-$CF(CF_3)$-CF_3	HFC-*b*-338mym	65781-19-3	14.65	15.34	325.4	0.272	3319	1211	2789	717	194
CH_3-$CF(CF_3)$-CF_3	HFC-*b*-347mym	662-00-0	36.79	39.54	528.5	0.294	5565	3372	5445	3414	1384
CH_2F-$CH(CF_3)$-CF_3	HFC-*b*-347mzm	2794-16-3	4.65	4.83	125.3	0.271	1531	422	806	86	59
CH_2F-$CF(CF_3)$-CHF_2	HFC-*b*-347myp	65781-22-8	8.70	9.08	205.0	0.268	2579	780	1830	253	110
CHF_2-$CH(CF_3)$-CHF_2	HFC-*b*-347mzp	65781-25-1	7.03	7.33	174.2	0.330	2685	776	1739	203	109
CHF_2-$CF(CHF_2)$-CHF_2	HFC-*b*-347pyp	65781-24-0	7.39	7.71	181.1	0.317	2688	784	1781	215	110
CH_3-$CH(CF_3)$-CF_3	HFC-*b*-356mzm	382-09-2	12.00	12.62	243.8	0.273	3624	1215	2880	577	180
CH_3-$CF(CF_3)$-CHF_2	HFC-*b*-356myp	65781-20-6	10.66	11.19	224.8	0.296	3632	1167	2779	481	169
CH_2F-$CH(CF_3)$-CHF_2	HFC-*b*-356mzp	32931-17-2	3.51	3.65	96.9	0.262	1252	342	572	64	47
CH_2F-$CF(CF_3)$-CH_2F	HFC-*b*-356myq	161791-34-0	7.03	7.34	166.7	0.252	2275	657	1474	172	92
CHF_2-$CH(CHF_2)$-CHF_2	HFC-*b*-356pzp	138507-15-0	4.58	4.76	119.7	0.303	1867	514	975	104	72
CH_2F-$CF(CHF_2)$-CHF_2	HFC-*b*-356pyp	35274-04-5	6.15	6.41	150.6	0.270	2174	615	1320	145	86
CH_3-$CH(CF_3)$-CHF_2	HFC-*b*-365mzp	381-95-3	3.51	3.65	94.5	0.248	1325	362	605	68	50
CH_3-$CF(CF_3)$-CH_2F	HFC-*b*-365myq	119450-80-5	3.67	3.81	97.8	0.212	1184	323	552	62	45
CH_3-$CF(CHF_2)$-CHF_2	HFC-*b*-365pyp	65781-23-9	6.25	6.53	146.6	0.260	2381	675	1458	161	94
CH_2F-$CH(CF_3)$-CH_2F	HFC-*b*-365mzq	161791-30-6	0.70	0.72	25	0.150	160	44	50	7	6
CH_2F-$CH(CHF_2)$-CHF_2	HFC-*b*-365pzp	32864-57-6	2.60	2.69	74.1	0.240	953	259	382	47	36
CHF_2-$CF(CH_2F)$-CH_2F	HFC-*b*-365pyq	65781-27-3	4.01	4.17	104.7	0.192	1165	319	568	62	44
CF_3-$CF(CH_3)$-CH_3	HFC-*b*-374my	154381-59-6	6.42	6.72	144	0.205	2186	622	1356	151	87
CF_3-$CH(CH_3)$-CFH_2	HFC-*b*-374mz	161791-27-1	0.97	1.00	32	0.150	252	69	81	12	9
CHF_2-$CF(CH_3)$-CH_2F	HFC-*b*-374py	65781-26-2	2.92	3.03	79.7	0.169	855	233	359	43	32
CHF_2-$CH(CH_3)$-CHF_2	HFC-*b*-374pzp	161791-28-2	1.93	2.00	57.2	0.190	638	174	233	31	24
CH_2F-$CF(CH_2F)$-CH_2F	HFC-*b*-374qyq	65781-28-4	4.59	4.78	112.8	0.142	1119	308	585	62	43
CHF_2-$CH(CH_2F)$-CH_2F	HFC-*b*-374pzq	161791-29-3	1.64	1.70	49.9	0.150	428	116	150	20	16
CF_3-$CH(CH_3)$-CH_3	HFC-*b*-383mz	1550-49-8	0.99	1.02	32.2	0.136	271	74	87	13	10
CHF_2-$CF(CH_3)$-CH_3	HFC-*b*-383py	66587-76-6	3.80	3.95	95.4	0.148	1128	309	535	59	43
CHF_2-$CH(CH_3)$-CH_2F	HFC-*b*-383pz	66587-77-7	0.68	0.70	25	0.102	140	38	44	6	5
CH_2F-$CF(CH_3)$-CH_2F	HFC-*b*-383qy	161791-26-0	2.36	2.44	66.0	0.112	531	145	206	26	20
CH_2F-$CH(CH_2F)$-CH_2F	HFC-*b*-383qzq	66675-40-9	1.02	1.05	33.1	0.088	180	49	58	8	7
CH_2F-$CF(CH_3)$-CH_3	HFC-*b*-392qy	62126-92-5	1.20	1.24	37.5	0.074	212	58	70	10	8
CH_2F-$CH(CH_3)$-CH_2F	HFC-*b*-392qz	62126-93-6	0.33	0.34	25	0.044	35	9	10	2	1
CHF_2-$CH(CH_3)$-CH_3	HFC-*b*-392pz	62126-91-4	0.31	0.31	25	0.069	51	14	15	2	2
CH_2F-$CH(CH_3)$-CH_3	HFC-*b*-3-10-1q	359-00-2	0.09	0.09	25	0.011	3	1	1	0	0
CH_3-$CF(CH_3)$-CH_3	HFC-*b*-3-10-1sy	353-61-7	1.21	1.25	37.4	0.039	140	38	46	7	5

[a]The values reported in this work were obtained using methods consistent with the methods used to derive the WMO (2018) lifetimes and climate metrics: Radiative efficiency (RE) in units of W m^{-2} ppb^{-1}; Global Warming Potential (GWP) and time-horizon; and Global Temperature Potential (GTP) and time-horizon.

applied to all molecules to account for a stratospheric temperature correction.

Global warming potentials on the 20- and 100-year time horizons (T) were calculated relative to CO_2 using

$$\mathrm{GWP}(T) = \frac{\mathrm{RE}\tau[1 - \exp(-T/\tau_{\mathrm{Atm}})]}{\mathrm{Int}\,\mathrm{RF}_{\mathrm{CO_2}}(T)}$$

The integrated (Int) CO_2 radiative forcing term in the denominator is consistent with the GWP values reported in the WMO-2018[1] and IPCC-2013[17] assessments corresponding to a CO_2 abundance of 391 ppm. Therefore, values reported in this work can be compared directly to values reported in the WMO and IPCC assessments.

Global temperature change potentials were calculated for the 20-, 50-, and 100-year time horizons using the parameterizations given in the IPCC[17] Supporting Information section S8.13.

RESULTS AND DISCUSSION

Lifetime and Climate Metric Data. Tables 1−4 and the Supporting Information datasheets provide a summary of the lifetime, RE, GWP, and GTP results obtained in this study for C1 and C2, C3, linear-C4, and branched-C4 HFCs, respectively. Detailed individual datasheets for each HFC are given in the Supporting Information. The datasheets include OH and $O(^1D)$ rate coefficient results, a breakdown of partial and global lifetimes, and a comparison with literature and recommended values for all parameters where available. The results of this study are also presented in graphical form in Figures S1−S4 for the C1 and C2, C3, linear-C4, and branched-C4 HFCs, respectively. The shaded values in Tables 1−3 were taken from WMO-2018,[1] while the values derived using our computational methods are provided in the datasheets. As expected, many of the HFCs are potent greenhouse gases (note that all RE values discussed in this section are lifetime and stratospheric temperature adjusted values). In addition to HFC isomers having different reactivity (lifetimes), each isomer has a unique infrared absorption

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spectrum and, thus, a unique RE. The HFCs with the highest H atom content generally have lower REs due to weaker infrared absorption in the Earth's atmospheric window region as well as shorter atmospheric lifetimes (REs reported in Tables 1−4 are lifetime corrected values).

We need to keep in perspective the level of uncertainty in the lifetimes and climate metrics given in the recommended values taken from the WMO assessment and the values from the present work given in Tables 1−4. The absolute uncertainty in the climate metrics may be substantial. The overall uncertainty includes contributions from laboratory kinetic measurements, which can be measured to ∼5−10% accuracy, and infrared absorption spectra, which can be measured to within 2−5% accuracy. The RE determination parameterizations[16] (irradiance, lifetime correction, and stratospheric temperature correction) contribute an estimated additional 25% uncertainty, or greater. Therefore, for the best of circumstances, GWPs are expected to have absolute uncertainties of ∼30%. A comparison of relative metrics is expected to be more certain due to cancellation of errors. For example, the uncertainty in the CO_2 forcing and irradiance parameterization would mostly cancel in a relative comparison. The relative uncertainties are most likely in the 10−15% range, or less.

We have not attempted to evaluate the uncertainty for each individual HFC included in this study. The agreement between the recommended RE and GWP climate metrics for the compounds included in WMO-2018 and those calculated here is shown in Figures 2 and 3, respectively. Note that the

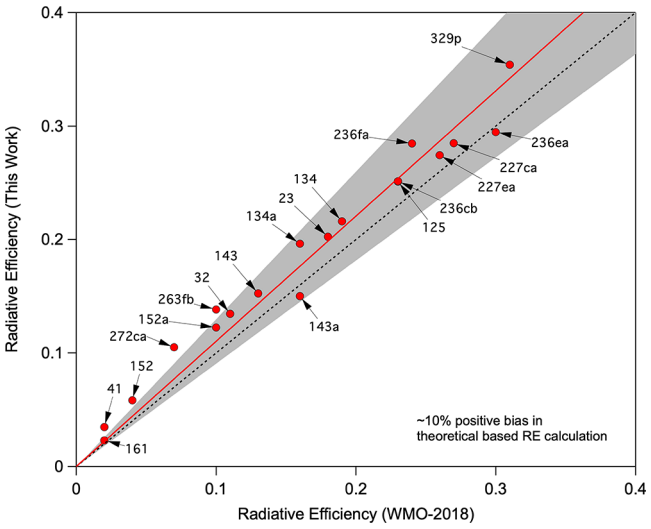

Figure 2. Comparison of hydrofluorcarbon (HFC) radiative efficiencies (REs) calculated in this work with those reported in WMO-2018.[1] The HFCs used in the comparison are labeled on the graph. The dashed line is the 1:1 relationship. The solid red line is an unweighted linear least-squares fit to the data that shows a 10% positive bias in the values obtained in this study. The edges of the gray shaded region represent the ±30% range around the fit line.

calculated metrics for HFC-23 are significant outliers due to the fact that the SAR does not reproduce the experimental OH reaction rate coefficient very well, as noted by DeMore.[6] Overall, the comparison of RE values is very good with only slight positive biases. The predominant atmospheric loss process for HFCs is reaction with the OH radical. The DeMore[6] SAR reproduces the experimentally measured room

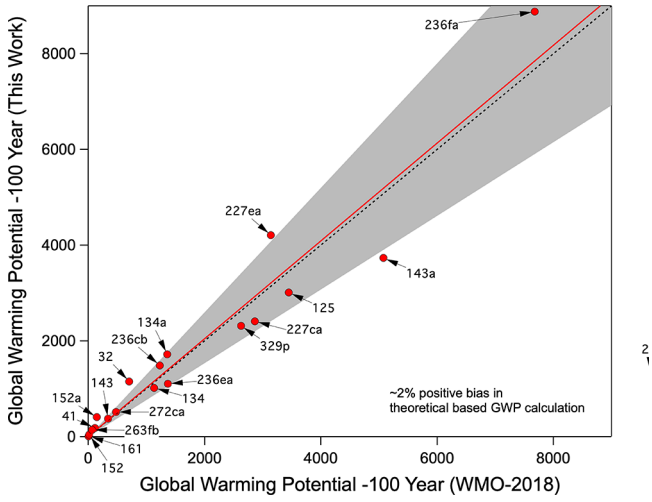

Figure 3. Comparison of hydrofluorcarbon (HFC) global warming potentials (GWPs) on the 100-year time horizon calculated in this work with those reported in WMO-2018.[1] The HFCs used in the comparison are labeled on the graph. Note that the data point for HFC-23 falls well off the line and is not shown (see the SI datasheet for HFC-23 for values). The dashed line is the 1:1 relationship. The solid red line is an unweighted linear least-squares fit to the data shown that shows a 2% positive bias in the values obtained in this study. The edges of the gray shaded region represent the ±30% range around the fit line.

temperature OH rate coefficients to within ∼30%. We have conservatively estimated the uncertainty in $k(272\ \mathrm{K})$ to be ∼50%. The uncertainty in the OH rate coefficient translates directly to the uncertainty in the HFC tropospheric lifetime. The theoretically derived REs agree to within ∼10% on average with the values derived using the experimentally measured spectra. As stated earlier, we estimated the uncertainty in the computed band strengths to be between 5% and 20% high, which is consistent with the theoretically determined REs in Figure 2 having ∼10% positive bias. For compounds with a lifetime of 0.2 to 1 year, i.e., those that fall on the steep portion of the lifetime correction profile given in Hodnebrog et al.,[16] additional significant uncertainty is introduced.

Figure 3 shows a comparison of the theoretically derived GWPs(100) and those reported in WMO-2018. As expected, since the theoretically based REs exhibit ∼10% positive bias, the computationally based GWPs(100) show a slight positive bias, in this case only ∼2%, which is better than should be expected. We conservatively estimate the climate metrics given in Tables 1−4 to have uncertainties within a factor of 1.5 to 2, primarily depending on the lifetime of the HFC, i.e., compounds with a shorter lifetime are expected to have metrics with a greater degree of uncertainty.

Trends in HFC Metrics. Tables 1−4 show that, in general, the substitution of F for H results in reduced OH radical reactivity, which is consistent with the enhancement factors in the OH reactivity SAR.[6] The reduced OH reactivity leads to longer atmospheric lifetimes. Increased fluorination also leads to stronger infrared absorption in the Earth's atmospheric window and greater well-mixed REs. The combination of low reactivity and enhanced RE leads to greater GWPs.

Notable exceptions to this general behavior are HFCs that contain a CH_3 terminal group bonded to a perfluorinated moiety. Two examples are CH_3CF_3 (HFC-143a) and

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$CH_3CF_2CF_3$ (HFC-245cb) for which there are experimental data and recommendations given in the WMO ozone assessment.[1] Although HFC-143a is not the most fluorinated C2 HFC, it has the longest atmospheric lifetime and largest GWP of all the C2 HFCs. Similarly, HFC-245cb has the second highest atmospheric lifetime and GWP of the C3 HFCs (this holds true for both GWP(20) and GWP(100)). This behavior is also evident for the C4 linear and branched molecules. There are experimentally based metrics for only one C4 linear molecule, $CHF_2CF_2CF_2CF_3$ (HFC-329p), so the comparisons discussed here are mostly based on the data from this study. The C4 linear molecule with the longest atmospheric lifetime and largest GWP is $CF_3CHFCF_2CF_3$ (HFC-329me), whereas the molecule with the third largest lifetime and GWP is $CH_3CF_2CF_2CF_3$ (HFC-347mcc), though we will note that the lifetime and GWP are only slightly larger than for $CHF_2CF_2CF_2CF_3$ (HFC-329p), which has metrics in Table 3 taken from WMO. For the C4 branched HFCs, there are no molecules included in WMO. In this case, the HFC with the largest lifetime and GWP is $CF_3CH(CF_3)CF_3$ (HFC-*b*-329mz) and the molecule with the second largest lifetime and GWP is $CH_3CF(CF_3)CF_3$ (HFC-*b*-347mym). This is, again, consistent with the observation that a terminal CH_3 group attached to a perfluorinated moiety leads to a greater lifetime and GWP.

A second observation is that the atmospheric lifetime is more important than the RE for a group of HFCs with a similar number of C and F atoms. That is, the OH reactivity has a stronger dependence on fluorination than the infrared absorption spectrum. For the C2 HFCs, the lifetime adjusted RE is largest for CHF_2CF_3 (HFC-125), 0.23. However, as noted above the C2 molecule with the largest GWP is CH_3CF_3 (HFC-143a), which has a RE of 0.16. For the C3 HFCs, the molecule with the second largest GWP, $CH_3CF_2CF_3$ (HFC-245cb), has a RE of 0.24, which is tied for only the fourth highest RE for all of the C3 HFCs. This trend continues for the C4 HFCs. The linear C4 HFC with the third highest GWP, $CH_3CF_2CF_2CF_3$ (HFC-347mcc), has a RE of 0.25, and this is not even in the top ten REs for the linear C4 HFCs. For the branched C4 HFCs, the molecule with the second largest GWP, $CH_3CF(CF_3)CF_3$ (HFC-b-347mym), has a RE of 0.29, and this is only the ninth largest RE for the branched C4 HFCs. Previously, Bera et al.[18] focused on the RE of HFCs as an important component that industry should consider when deciding what particular HFC to use in an industrial process. The data in Tables 1−4 support their assertion, but also indicates that the HFC atmospheric lifetime is a more important aspect to consider.

It is evident from an examination of the metrics given in WMO for the C3 HFCs in Table 2 that for HFCs with the same empirical chemical formula, i.e., isomers, those that do not have H atoms on the terminal C atoms have longer lifetimes and larger GWPs. There is one exception as noted above when there are three H atoms and all on a terminal C, i.e., a CH_3 group. Consider for example the empirical formula $C_2H_2F_6$. $CF_3CH_2CF_3$ (HFC-236fa) has the largest atmospheric lifetime at 213 years and the largest GWP of all C3 HFCs. For the empirical formula $C_2H_3F_5$, aside from $CH_3CF_2CF_3$ (HFC-245cb) discussed above, the HFC with the next largest lifetime and GWP is $CHF_2CH_2CF_3$ (HFC-245fa) consistent with this observation. Note also that $CHF_2CH_2CF_3$ (HFC-245fa) is tied for the largest RE for the $C_2H_3F_5$ HFCs, consistent with the observations of Bera et al.[2,18] This trend continues for the C4 HFCs studied here, where the linear C4 HFC with the longest lifetime by far and the largest GWP is $CF_3CH_2CF_2CF_3$ (HFC-338mf). However, to some extent this is to be expected, since, as noted earlier, most of the atmospheric lifetimes for the C4 HFCs are computed in this study using the OH reaction rate coefficients determined from the structure activity relationship (SAR) developed by DeMore.[6]

In summary, the larger the number of F atoms in a particular HFC, the greater the likelihood that HFC will possess a longer atmospheric lifetime, a large RE, and thus a large GWP. However, how the F atoms are distributed around the HFC, i.e., isomers, will determine how large the RE is, but more importantly, how long the atmospheric lifetime is, and ultimately the GWP.

CONCLUSIONS

In this study, policy relevant metrics have been provided for HFC compounds with fewer than 5 carbon atoms (153 compounds in total) most of which lack direct experimentally derived metric values. Tables 1−4 summarize the results from this study and detailed datasheets for the individual HFCs are provided in the Supporting Information. We have demonstrated that HFCs with different chemical formulas and the associated isomers have significantly different atmospheric lifetimes and climate metrics. That is, reliable lifetimes and climate metrics cannot be assigned based on the empirical chemical formula alone.

We have shown that both the radiative efficiency (RE) and the atmospheric lifetime of an HFC are important parameters in determining a molecule's potential environmental impact, but the atmospheric lifetime is generally more important than the RE in the GWP determination for most HFCs. To some extent, the degree of fluorination, lifetime, and RE are correlated. This is because HFCs react more readily with OH when they possess more H atoms and the RE is lower because the RE is mostly determined by the number of C−F stretching vibrations, which absorb in the Earth's atmospheric infrared window. However, we have shown that there are exceptions, since HFCs that have a CH_3 terminal group bonded to essentially a perfluorinated moiety lead to an HFC with a very long atmospheric lifetime and a large GWP, even if the RE of that particular HFC is not as large as some of the others in its class (isomers). For example, for the C4 HFCs, $CH_3CF_2CF_2CF_3$ (HFC-347mcc) exhibits a larger GWP and longer lifetime than all but two linear C4 HFCs, but its RE is not even in the top ten for the linear C4 HFCs.

Many of the C3 and most of the C4 HFC atmospheric lifetimes and climate metrics reported here were determined using the computational methods described herein: that is, a structure activity relationship (SAR) based approach for determining OH reactivity and, thus, atmospheric lifetimes and *ab initio* MP2 computed vibrational spectra that were used in the RE determination. A comparison of the computed REs for the C2 and C3 HFCs with the values reported in the WMO ozone assessment[1] showed that the computationally based REs exhibit ∼10% positive bias, in part due to the calculated infrared intensities being between 5% and 20% too large. It is important to note that the data reported herein are not a substitute for accurate detailed experimental studies of targeted compounds prior to their commercial use. However, the data reported here will help guide future experiments, particularly

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when it is difficult to separate isomers, and provide relevant information to policy decision makers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c02679.

Summary graphs of HFC climate metrics (PDF)
Data sheets for HFCs (C1) (PDF)
Data sheets for HFCs (C2) (PDF)
Data sheets for HFCs (C3) (PDF)
Data sheets for HFCs (linear-C4) (PDF)
Data sheets for HFCs (branched-C4) (PDF)

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Notes

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