

Updated radiative forcing estimates of 65 halocarbons and nonmethane hydrocarbons

Article

Published Version

Sihra, K., Hurley, M. D., Shine, K. P. and Wallington, T. J. (2001) Updated radiative forcing estimates of 65 halocarbons and nonmethane hydrocarbons. *Journal of Geophysical Research - Atmospheres*, 106 (D17). pp. 20493-20505. ISSN 0148-0227 doi: <https://doi.org/10.1029/2000JD900716> Available at <http://centaur.reading.ac.uk/35103/>

It is advisable to refer to the publisher's version if you intend to cite from the work.

Published version at: <http://dx.doi.org/10.1029/2000JD900716>

To link to this article DOI: <http://dx.doi.org/10.1029/2000JD900716>

Publisher: American Geophysical Union

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

Updated radiative forcing estimates of 65 halocarbons and nonmethane hydrocarbons

Kamaljit Sihra,¹ Michael D. Hurley,² Keith P. Shine,¹
and Timothy J. Wallington²

Abstract. The direct radiative forcing of 65 chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, hydrofluoroethers, halons, iodoalkanes, chloroalkanes, bromoalkanes, perfluorocarbons and nonmethane hydrocarbons has been evaluated using a consistent set of infrared absorption cross sections. For the radiative transfer models, both line-by-line and random band model approaches were employed for each gas. The line-by-line model was first validated against measurements taken by the Airborne Research Interferometer Evaluation System (ARIES) of the U.K. Meteorological Office; the computed spectrally integrated radiance of agreed to within 2% with experimental measurements. Three model atmospheres, derived from a three-dimensional climatology, were used in the radiative forcing calculations to more accurately represent hemispheric differences in water vapor, ozone concentrations, and cloud cover. Instantaneous, clear-sky radiative forcing values calculated by the line-by-line and band models were in close agreement. The band model values were subsequently modified to ensure exact agreement with the line-by-line model values. Calibrated band model radiative forcing values, for atmospheric profiles with clouds and using stratospheric adjustment, are reported and compared with previous literature values. Fourteen of the 65 molecules have forcings that differ by more than 15% from those in the *World Meteorological Organization* [1999] compilation. Eleven of the molecules have not been reported previously. The 65-molecule data set reported here is the most comprehensive and consistent database yet available to evaluate the relative impact of halocarbons and hydrocarbons on climate change.

1. Introduction

The Kyoto Protocol calls for international limits on the emission of greenhouse gases such as CO₂, N₂O, CH₄, HFCs, and SF₆. To compare the relative impact of different greenhouse gas control strategies, it is necessary to place the climatic impacts of various greenhouse gases on a common scale. For any meaningful scale, knowledge of the radiative forcing for each gas is required. As a result of the Montreal Protocol a large number of different compounds are under consideration as replacements for chlorofluorocarbons. In comparing the environmental impacts of these replacements, it is necessary to consider their potential effect on global climate. Over the past 5-10 years, there have been

many studies which have reported cross-sectional measurements and radiative forcing calculations for possible CFC replacements [e.g., *Christidis et al.*, 1997; *Clerbaux et al.*, 1993; *Good et al.*, 1998; *Hansen et al.*, 1997; *Heathfield et al.*, 1998; *Imasu et al.*, 1995; *Ko et al.*, 1999; *Myhre et al.*, 1998; *Naik et al.*, 2000; *Pinnock et al.*, 1995; *Roehl et al.*, 1995]. Unfortunately, typically only a few gases are studied in each investigation, and there are often significant differences in the methodologies used in the different studies (e.g., different absorption spectra, radiative transfer models and different atmospheric profiles of the most abundant gases). Comparison of radiative forcing values reported from different laboratories is often not a straightforward process. A consistent and comprehensive set of well-documented forcing calculations is needed to provide a clear relative ranking of the potential climatic impacts of the large number of potential CFC replacements. The most comprehensive study to date is that of *Jain et al.* [2000], who report results for 39 gases by combining distributions calculated with a two-dimensional chemical transport model with detailed radiative transfer calculations.

In this study we have undertaken a systematic study of the infrared spectra and radiative forcing of 65 halo-

¹Department of Meteorology, University of Reading, Reading, England, United Kingdom.

²Ford Motor Company, Dearborn, Michigan.

Copyright 2001 by the American Geophysical Union.

Paper number 2000JD900716.

0148-0227/01/2000JD900716\$09.00

carbons and hydrocarbons, 11 of which have not been reported to our knowledge. To maximize the experimental precision, the infrared spectra of all of the compounds (except CFC-11, HFC-245fa, perfluorocyclobutane, trichloromethane, and 1,2 dichloromethane) were measured using the same experimental techniques and apparatus [Pinnock *et al.*, 1995]. Two different radiative transfer models were utilized for each of the gases in order to quantify the impact of the model on the radiative forcing result.

Radiative transfer calculations performed using the line-by-line approach were carried out using a modified version of the Reference Forward Model (RFM) [Dudhia, 1997], a fast forward model based on the GENLN2 model [Edwards, 1987]. The RFM was compared with other line-by-line models from the Intercomparison of Radiation Codes Used in Climate Models (ICRCCM) and validated against observations by the Airborne Research Interferometer Evaluation System (ARIES) of the U.K. Meteorological Office. A discussion of the results is given in section 2.

Absorption spectra were measured over the 450 to 2000 cm^{-1} range to include not only the main spectral signatures typically found between 700 and 1500 cm^{-1} , but also the generally smaller features which are present in the 450 to 700 cm^{-1} spectral range. The 700 and 1500 cm^{-1} region is important since the principal gases found in the atmosphere absorb most weakly within this range. The 450 to 700 cm^{-1} region, encapsulating strong surface emissions but also strong absorption bands of water vapor and carbon dioxide, is less important [Pinnock *et al.*, 1995]. However, for gases such as toluene, with 7.1% of the integrated cross section falling in the 450 to 600 cm^{-1} range that contributes 16.5% to the radiative forcing, this frequency range is certainly significant. The infrared spectra, the integrated absorption cross sections, and a discussion on contaminants are given in section 4.

The impact of these gases on the atmosphere is quantified by their “adjusted radiative forcing” [Intergovernmental Panel on Climate Change (IPCC), 1995],

which is defined as the net change in irradiance at the tropopause from the inclusion of a greenhouse gas, after the stratospheric temperatures have been allowed to adjust to this change and return to a radiative equilibrium. To include clouds and stratospheric adjustment is computationally expensive for the line-by-line model. Hence the clear-sky “instantaneous radiative forcing,” which does not include stratospheric adjustment, is also used for each gas to calibrate a narrowband model which is used for the calculation of the adjusted forcings. No previous study has used line-by-line calculations for such a large number of gases. A discussion of the models, radiative forcings, global warming potentials (GWPs), and a comparison with other values found in the literature concludes this study.

2. Validation of the Reference Forward Model

Line-by-line model calculations were performed using the Reference Forward Model (RFM) [Dudhia, 1997]. The irradiance calculation was included using a four-point Gaussian quadrature that approximates the zenith angle integration to better than 0.1% [Clough *et al.*, 1992]. This flux form of the model, hereinafter referred to as the FRFM, was run at a spectral resolution of 0.0025 cm^{-1} , which is sufficient to resolve Lorentz broadened lines from near the surface to the upper stratosphere. The ability to resolve lines above this height was found to produce a negligible change in downward irradiance to the tropopause. The HITRAN 1996 line compilation [Rothman *et al.*, 1998], “CKD2.1” water vapor continuum [Clough *et al.*, 1992], and a line wing limit of 25 cm^{-1} were also used for all model calculations. Furthermore, for each vertical profile layer, the Planck function was permitted to vary linearly with optical depth so that in the extremes, the radiance (or irradiance) from a layer boundary represented the temperature of that boundary at opaque frequencies and the mean layer temperature at optically thin frequencies [see, e.g., Wiscombe, 1976; Clough *et al.*, 1992]. This

Table 1. Comparison of Line-by-Line Models for Three Atmospheric Cases^a

	Tropical			Midlatitude Summer			Subarctic Winter		
	F_{sfc}	F_{trp}	F_{toa}	F_{sfc}	F_{trp}	F_{toa}	F_{sfc}	F_{trp}	F_{toa}
ICRCCM									
Minimum	389.92	277.62	290.26	343.07	265.00	283.32	164.44	178.08	202.61
Maximum	397.86	288.14	294.40	351.19	274.53	290.47	166.73	179.92	203.45
FGENLN2	395.49	281.69	292.63	347.49	266.58	283.59	171.17	172.86	199.83
LBLRTM	394.66	277.62	290.26	346.91	265.30	283.32			
FRFM	396.86	277.72	290.70	348.10	265.51	283.90	170.73	173.88	200.59

^aIrradiances are given in W m^{-2} , where F_{sfc} is the downward irradiance at the surface, F_{trp} is the net upward irradiance at the tropopause, and F_{toa} is the upward irradiance at the top of the atmosphere. Abbreviations are ICRCCM, Intercomparison of Radiation Codes Used in Climate Models; FGENLN2, Flux version of the GENLN2 line-by-line model; LBLRTM, Atmospheric Environment Research line-by-line model; and FRFM, flux Reference Forward Model.

more realistic representation was also used in all of the model calculations. The model validation was carried out in two parts: a comparison with other line-by-line models and a validation against observations.

2.1. Model Comparison

The model comparison was performed using archived data from the four line-by-line modeling groups in the ICRCM comparison [Ellingson *et al.*, 1991]. The data were obtained from the Carbon Dioxide Information Analysis Center Web site (http://cdiac.esd.ornl.gov/ftp/ICRCM-radiative_fluxes). The range of irradiances for these models is shown in Table 1 for three atmospheric profiles: tropical, midlatitude summer, and subarctic winter (ICRCM cases 25, 27, and 33, respectively). For each case, vertical concentration profiles of water vapor, ozone, and carbon dioxide were also given (CO_2 with a uniform concentration of 300 ppmv). Irradiances from the Atmospheric Environment Research line-by-line model (LBLRTM) are shown explicitly, since this is closest in formulation to the FRFM, and those from the flux version of the GENLN2 model (FGENLN2), previously at Reading [Pinnock and Shine, 1998], are also included for comparison.

The range of ICRCM values is much greater for the tropical and midlatitude summer cases than for the subarctic winter. The profile for the latter case has a much lower surface temperature and a much weaker vertical structure, which make differences, particularly from the type of water vapor continuum model used, less significant. Differing line wing limits, spectral databases, vertical resolution, and in one model, slightly different mixing ratios, all contribute to the variability. For the tropical and midlatitude summer cases the FRFM irradiances lie within the ICRCM range. For subarctic winter, the models run with a greater number of approximations tend toward weaker absorption (emission) than the FRFM and FGENLN2. More important, for all three cases, the FRFM agrees to better than 1.5% with the LBLRTM and FGENLN2 model irradiances. The instantaneous, clear-sky radiative forcings for a doubling of carbon dioxide concentration from 300 to 600 ppmv for the midlatitude summer case are 5.55 W m^{-2} for the FRFM, 5.59 W m^{-2} for the LBLRTM model, and 5.54 W m^{-2} for FGENLN2. These values are consistent within 1%, which is an acceptable level of agreement given the differences between the models. The average of the ICRCM line-by-line models gives a forcing of 5.63 W m^{-2} , which is somewhat higher than the FRFM value. However, the ICRCM average is biased by the models calculating weaker absorptions, for example, by using line wing limits of 10 cm^{-1} instead of 25 cm^{-1} . For these models the increase in CO_2 concentration from 300 to 600 ppmv results in the strongly absorbing CO_2 band centered at 667 cm^{-1} ($15 \mu\text{m}$) to saturate in transmittance. Since this band is already partially saturated at 300 ppmv in

the more comprehensive models such as the LBLRTM and FRFM, the change in irradiance, and hence forcing, is less pronounced.

2.2. Comparison With Observations

A validation of the model, however, can necessarily be achieved only by a comparison with observations. In this case, radiance measurements were used that were recorded by the ARIES instrument and provided by J. P. Taylor (personal communication, 1999). The ARIES instrument is a thermal infrared interferometer capable of recording in either the zenith or nadir over an altitude range of 30–9000 m. Validation was performed across the 700 to 3000 cm^{-1} spectral range at 0.5 cm^{-1} resolution. The tropospheric temperature and concentration profiles of water vapor and ozone were provided from in situ measurements on board the aircraft. The stratospheric profiles were taken from the global and multiannual atmosphere of Christidis *et al.* [1997]. Uniform vertical profiles of carbon dioxide (358 ppmv), methane (1720 ppbv), nitrous oxide (312 ppbv), and carbon monoxide (137 ppbv) were included to represent the present-day atmosphere. Figure 1a shows an ARIES zenith spectrum recorded at midlatitude in October 1998, Figure 1b shows the calculated result, and Figure 1c shows the residuals (ARIES minus RFM).

The model shows excellent agreement with observations across the entire spectral range, with frequency-integrated radiances of $48.45 \text{ W m}^{-2} \text{ sr}^{-1}$ for the ARIES instrument and $47.65 \text{ W m}^{-2} \text{ sr}^{-1}$ for the RFM, a difference of 1.7%, not including the negative radiances between 2500 and 3000 cm^{-1} and instrument noise between 1400 and 1800 cm^{-1} . A comparison of an ARIES spectrum measured in the nadir was also performed. The frequency-integrated radiances showed a smaller difference (better than 0.5%), which is expected since nadir spectra show less sensitivity to spectral differences given the surface emission term. The agreement between the measured and modeled data in Figure 1 provides a validation of the RFM line-by-line model.

3. The Radiative Transfer Models

The FRFM is not able to include clouds or stratospheric adjustment. The narrowband model (NBM) of Shine [1991] is therefore used to calculate instantaneous cloud-free forcings, for comparison against the FRFM, as well as the cloudy, adjusted forcings. The line-by-line approach employs the most fundamental physics and high numerical accuracy to evaluate the radiative transfer equations. It is therefore thought to be the most accurate atmospheric radiative transfer model subject to the limiting and significant caveats of imprecise spectral line parameters and line shape. Hence the forcings from the FRFM are used to calibrate those from the NBM; the cloudy, adjusted forcings are scaled directly by a gas-dependent scale factor so that the instanta-

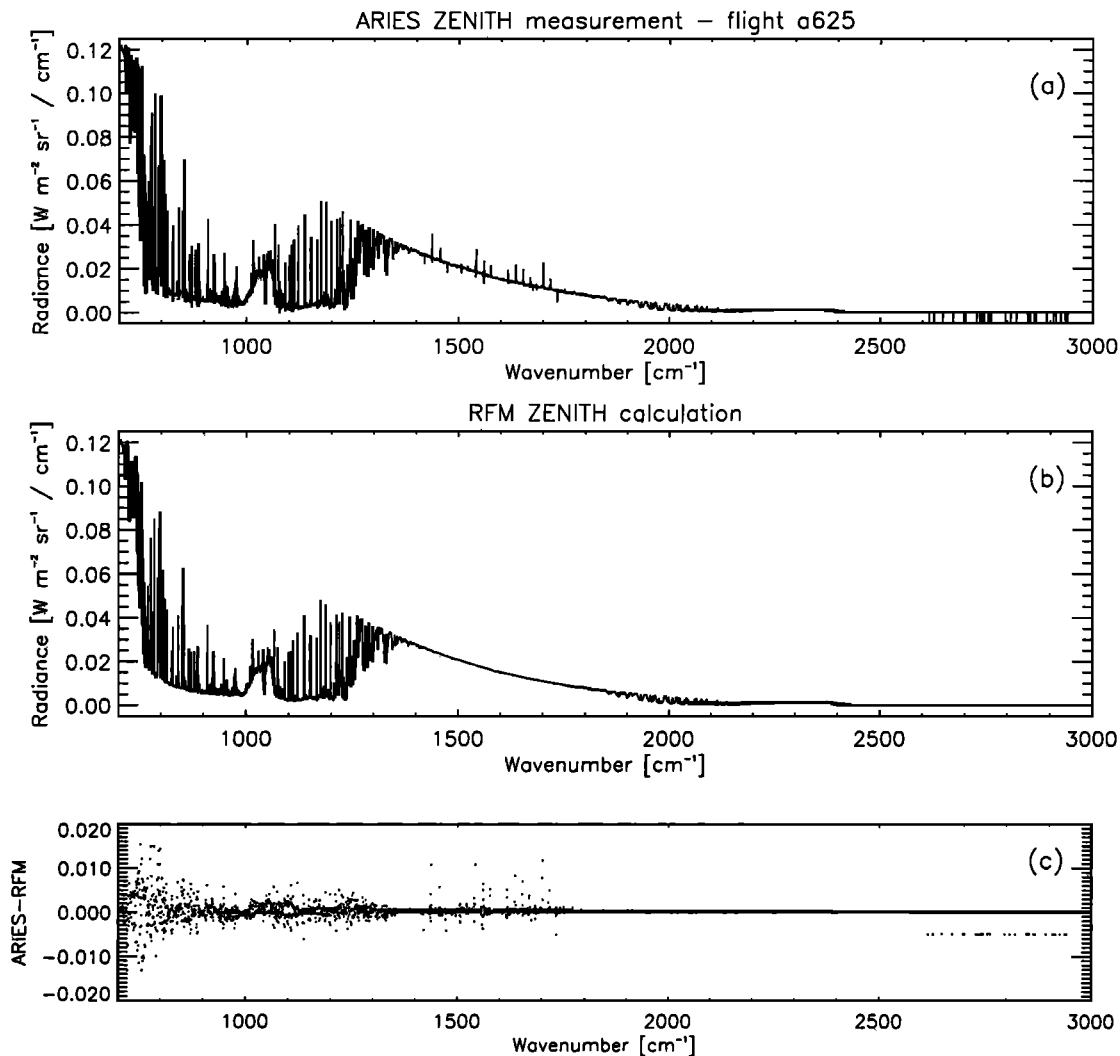


Figure 1. An Airborne Research Interferometer Evaluation System (ARIES) zenith spectrum recorded at midlatitude in October 1998 over the 700 to 3000 cm^{-1} spectral range is shown in Figure 1a. The corresponding Reference Forward Model (RFM) calculated spectrum is shown in Figure 1b. The spectrally integrated radiances are $48.45 \text{ W m}^{-2} \text{ sr}^{-1}$ for the ARIES instrument and $47.65 \text{ W m}^{-2} \text{ sr}^{-1}$ for the RFM.

neous, clear-sky forcings from the NBM agree exactly with those from the FRFM. The NBM has a spectral resolution of 10 cm^{-1} , with 250 bands across the 0 to 2500 cm^{-1} range. The model uses the Malkmus statistical distribution of line strengths [Malkmus, 1967] since this “model” more closely represents reality than any of the other random band models. Transmittances are calculated using either the HITRAN 1996 database or absorption cross sections for the halocarbons, averaged into 10 cm^{-1} intervals and the CKD 2.1 water vapor continuum model. Irradiances are calculated again using four-point Gaussian quadrature. Both models sub-layer the vertical profiles so that variations in the Planck function can be neglected. Three cloud layers can be included in the atmospheric profile using a basic parameterization of optical depth, with the fractional coverage of each cloud layer taken from the International

Satellite Cloud Climatology Project (ISCCP) and with the uppermost cloud tuned to give an agreement of approximately 1% with observed outgoing longwave radiation at the top of the atmosphere [Freckleton *et al.*, 1998]. Stratospheric adjustment was included by assuming that the combination of constant solar heating rate and dynamical heating balances the infrared cooling rate and using an iterative technique to adjust the stratospheric temperatures until the radiative equilibrium, upset by the inclusion of the new molecule, is restored [Pinnock *et al.*, 1995].

Atmospheric profiles of temperature, cloud cover, and water vapor and ozone concentrations were used to represent the tropics and the extratropics of each hemisphere (as described by Freckleton *et al.* [1998]). The profiles were based on multiyear averages of European Centre for Medium-Range Weather Forecasts (ECMWF)

analyses and combinations of different satellite instrument data (see *Christidis et al.* [1997] for a more complete description). Uniform profiles of carbon dioxide (358 ppmv), methane (1720 ppbv), and nitrous oxide (312 ppbv) were used. The tropopause height was defined as the “conventional” thermal tropopause [*World Meteorological Organization (WMO)*, 1986]. The background concentration of the trace gases was assumed to be zero, with forcings calculated for a 0.1 ppbv uniform increase in concentration. The global mean forcing is hence calculated by area-weighting the three forcings and linearly scaling to 1.0 ppbv. This ensures that no sharp spectral features saturate and that absorptions remain within the regime of the weak limit, one of the regimes where the NBM most accurately calculates transmittance [see *Pinnock et al.*, 1995]. This method is also more appropriate to calculate radiative forcings of trace gases for observed or anticipated atmospheric concentrations which are typically much lower than 1.0 ppbv. A significant error arises from the assumption of a uniform profile for short-lived gases. For this study we use correction factors from *Jain et al.* [2000] for gases common to our studies; for other gases we use a lifetime-dependent factor based on the results of *Jain et al.* [2000] to account simply for the impact of atmospheric lifetime. The validity of this method is discussed in section 5. Note that *Jain et al.* [2000] also calculate the forcing using the full latitudinal and seasonal variations in background conditions; the full profiles give a forcing typically 2–3% higher than for a global mean profile, reaching 7% for a few gases. As discussed later, such errors are no bigger than other sources of error, such as in absorption cross section or specification of tropopause position.

4. Integrated Absorption Cross Sections

Absorption cross-sectional spectra were measured at the Ford Motor Company, with additional spectra obtained from the Spectroscopy and Warming Potentials of Atmospheric Greenhouse Gases (SWAGG) project [*Highwood and Shine*, 2000] and from *Clerboux et al.* [1993]. The spectra of CFC-12 from HITRAN 1996 [*Varanasi and Nemtchinov*, 1994] and HFC-245fa (reported by *Ko et al.* [1999]) were also included; the gases measured by each of these sources, and their integrated cross sections, are shown in Table 2. Where possible, the cross sections were recorded across the 450 to 2000 cm^{-1} spectral range; details of the Ford experimental setup are given by *Christidis et al.* [1997]. Forty-four of the trace gases and their forcings calculated using this NBM have been reported by our group previously [*Pinnock et al.*, 1995; *Christidis et al.*, 1997; *Highwood et al.*, 1999; *Highwood and Shine*, 2000]. Eleven of the trace gases have not been previously reported to our knowledge. For completeness, in addition to the new measurements of infrared spectra for the hydrofluoroethers, halons, and perfluorocarbons listed in Ta-

ble 2, we also ran checks of the infrared spectra of the 44 compounds (hydrofluorocarbons, hydrochlorofluorocarbons, and nonmethane hydrocarbons) that we had previously measured [*Pinnock et al.*, 1995; *Christidis et al.*, 1997; *Highwood et al.*, 1999], some of which had been used by *Naik et al.* [2000] and *Jain et al.* [2000].

In the process of double checking the old spectra, we found there was a small shift in the baseline of 13 of the old spectra. Accordingly, we remeasured the infrared spectra of all of the gases and report the new results given in Table 2. After remeasurement, we found that seven of the 44 spectra had integrated cross sections which were more than 10% different from our published measurements. These compounds are indicated in Table 2. Smaller corrections are also made to some of the other gases. A small proportion of the infrared spectra were contaminated with water vapor lines between 1400 and 2000 cm^{-1} , which arise because of traces of water vapor in the infrared beam within the spectrometer. A Kalman filtering technique [*Kalman*, 1960] was used effectively to remove water lines to within the level of the noise (for a complete description of this method see *Sihra* [1998]).

5. Radiative Forcings and Global Warming Potentials

5.1. The Effect of Nonuniform Vertical Profiles

The adjusted, cloudy-sky, global, and annual mean radiative forcings are shown in Table 3, for uniform 1.0 ppbv vertical profiles and taking into account atmospheric lifetimes. These uniform 1.0 ppbv values are regarded as reference values, as these allow a more ready comparison between different studies. The 1.0 ppbv values will overestimate the forcing because of the falloff in concentrations above the tropopause. For some trace gases, notably CFC-11 and CFC-12, some observations exist with which to characterize the impact of nonuniform distributions [e.g., *Freckleton et al.*, 1998]. For others, 2-D chemical transport models can be used to deduce vertical profiles [see, e.g., *Freckleton et al.*, 1998; *Naik et al.*, 2000; *Jain et al.*, 2000]. Such an approach is clearly the most comprehensive, but the lack of data with which to evaluate such models, particularly for the shorter-lived species, and the difficulties in representing transport, especially in 2-D models, must be recognized. In addition, assumptions have to be made about the distributions of emissions (e.g., *Freckleton et al.* [1998] assumed emissions to be predominantly in the Northern Hemisphere, while *Naik et al.* [2000] and *Jain et al.* [2000] specify a constant surface mixing ratio everywhere). Furthermore, an assumption has to be made about whether the model is run to a steady state. As an example of the problems in using model-derived vertical profiles, *Naik et al.* [2000] report that the CFC-11 model-derived forcing is 11% smaller than for a constant profile case; *Freckleton et al.* [1998] used

Table 2. Integrated Absorption Cross Sections Over the Range 450-2000 cm^{-1} Measured in the Present Work at 296 K (Ford Motor Company) and Previous Results From *Clerbaux et al.* [1993] and the Spectroscopy and Warming Potentials of Atmospheric Greenhouse Gases Project (SWAGG)^a

Gas	Chemical Formula	Integrated Cross Section ($10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$)		
		Ford	<i>Clerbaux et al.</i> [1993]	SWAGG
CFC-11	CCl_3F	9.31		
CFC-12 ^b	CCl_2F_2	13.59		
HCFC-123	CHCl_2CF_3	11.99 ^c	12.17	
HCFC-124	CHClFCF_3	13.85 ^c	(14.43)	
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$	7.14 ^c	6.84	
HCFC-142b	CH_3CClF_2	9.58 ^c	10.83	
HCFC-21	CHFCl_2	7.48		
HCFC-225ca ^d	$\text{CHCl}_2\text{CF}_2\text{CF}_3$	18.41 ^c	17.49	
HCFC-225cb	$\text{CClF}_2\text{CF}_2\text{CHClF}$	15.39 ^c	16.51	
HCFC-22	CHClF_2	10.16 ^c	9.98	10.23
HFC-125	CHF_2CF_3	16.47 ^c	(16.11)	16.73
HFC-134	CHF_2CHF_2	10.57		
HFC-134a	CFH_2CF_3	12.40 ^c	12.67	13.62
HFC-143	$\text{CHF}_2\text{CH}_2\text{F}$	7.14 ^c		
HFC-143a	CF_3CH_3	12.71 ^c		12.01
HFC-152a	CH_3CHF_2	6.87 ^c	7.07	6.70
HFC-161	$\text{CH}_3\text{CH}_2\text{F}$	2.46		
HFC-227ca	$\text{CF}_3\text{CF}_2\text{CHF}_2$	19.97		
HFC-227ea	$\text{CF}_3\text{CHF}_2\text{CF}_3$	23.04 ^c		
HFC-236cb	$\text{CF}_3\text{CF}_2\text{CH}_2\text{F}$	16.96		
HFC-236fa	$\text{CF}_3\text{CH}_2\text{CF}_3$	23.42 ^c		
HFC-23	CHF_3	11.61 ^c		[10.09]
HFC-245cb	$\text{CF}_3\text{CF}_2\text{CH}_3$	16.71		
HFC-245fa ^e	$\text{CF}_3\text{CH}_2\text{CHF}_2$	19.57		
HFC-272ca	$\text{CH}_3\text{CF}_2\text{CH}_3$	5.69 ^c		
HFC-32 ^d	CH_2F_2	5.65 ^c		5.62
HFC-41 ^d	CH_3F	1.57 ^c		
HFE-245fa2	$\text{CF}_3\text{CH}_2\text{OCHF}_2$	26.31		
HCFE-235da2	$\text{CF}_3\text{CHClOCHF}_2$	27.44		
HFE-125	CF_3OCHF_2	31.55		
HFE-143a	CF_3OCH_3	20.16		
HFE-356mff2	$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$	27.33		
HFE-7100	$\text{C}_4\text{F}_9\text{OCH}_3$	36.04		
HFE-7200	$\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$	36.56		
i7100	<i>i</i> - $\text{C}_4\text{F}_9\text{OCH}_3$	37.61		
n7100	<i>n</i> - $\text{C}_4\text{F}_9\text{OCH}_3$	33.71		
i7200	<i>i</i> - $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$	32.70		
H-Galden 1040X	$\text{CHF}_2\text{OCF}_2\text{OC}_2\text{F}_4\text{OCHF}_2$	65.82		
Halon 1211	CF_2BrCl	12.51		
Halon 2402	$\text{CF}_2\text{BrCF}_2\text{Br}$	15.40		
Halon 1301	CF_3Br	16.84		
Trifluoromethyl sulphur Pentafluoride	CF_3SF_5	25.44 ^c		
Perfluoromethane	CF_4	21.93		
Perfluoroethane	C_2F_6	21.68		22.81
Perfluoropropane	C_3F_8	27.39		
Perfluorocyclobutane	C_4F_8			21.56
Perfluorobutane	C_4F_{10}	31.41		
Iodopentafluoroethane	$\text{CF}_3\text{CF}_2\text{I}$	17.72		
Iodotrifluoromethane	CF_3I	15.47		
Dibromomethane	CH_2Br_2	2.07		
Difluorobromomethane	CHF_2Br	10.04		
Methyl bromide ^d	CH_3Br	0.71		
1,2 dichloroethane	$\text{CH}_2\text{ClCH}_2\text{Cl}$			[2.03]
Trichloromethane	CHCl_3			[5.08]
Acetylene ^d	C_2H_2	3.90		
Benzene ^d	C_6H_6	3.04		
Cyclohexane	C_6H_{12}	0.53		
Ethane	C_2H_6	0.38		
Ethene	C_2H_4	1.67		

Table 2. (continued)

Gas	Chemical Formula	Integrated Cross Section (10^{-17} cm ² molecule ⁻¹ cm ⁻¹)		
		Ford	<i>Clerbaux et al.</i> [1993]	SWAGG
n-butane ^d	C ₄ H ₁₀	0.63		
n-pentane	C ₅ H ₁₂	0.72		
Propane	C ₃ H ₈	0.54		
Propylbenzene	C ₆ H ₅ CH ₂ CH ₂ CH ₃	2.43		
Styrene	C ₆ H ₅ CHCH ₂	3.13		
Toluene	C ₆ H ₅ CH ₃	2.34		

^aWhere available, the 253 K data from the *Clerbaux et al.* [1993] and SWAGG studies are given; otherwise the spectra were recorded at 287 K [*Clerbaux et al.*, 1993] or 295 K (SWAGG), as indicated by values in parentheses and brackets, respectively. In the case of HCFC-22, the SWAGG spectrum was recorded at 273 K. Data for HFC-245fa were taken from *Ko et al.* [1999], and for CFC-12 the 259-K spectrum in HITRAN 1996 was used.

^bTaken from HITRAN (1996).

^cWavenumber range is 700–2000 cm⁻¹.

^dIntegrated absorption cross sections which differ from our previously published results by more than 10%.

^eTaken from *Ko et al.* [1999].

Table 3. Global, Annual Mean, Cloudy-Sky Radiative Forcings for a 1.0-ppbv Change in Trace Gas Mixing Ratio, for a Uniform Profile and Estimated for Lifetime-Dependent Profiles Based on the Results of *Jain et al.* [2000]^a

Gas	Radiative Forcing, W m ⁻² ppbv ⁻¹			
	Constant Profile	Lifetime Adjusted	WMO [1999]	<i>Jain et al.</i> [2000]
CFC-11	0.269	0.242	0.25	0.240
CFC-12	0.337	0.321	0.32	0.302
HCFC-123	0.192	0.141	0.20	0.143
HCFC-124	0.215	0.193	0.22	0.195
HCFC-141b	0.150	0.130	0.14	0.131
HCFC-142b	0.189	0.163	0.20	0.164
HCFC-21	0.173	0.140	0.17	
HCFC-225ca	0.259	0.202	0.27	0.207
HCFC-225cb	0.317	0.280	0.32	0.245
HCFC-22	0.213	0.208	0.22	0.205
HFC-125	0.236	0.223	0.23	0.249
HFC-134	0.193	0.180	0.18	0.176
HFC-134a	0.168	0.159	0.19	0.200
HFC-143	0.134	0.118	0.13	0.115
HFC-143a	0.154	0.148	0.16	0.160
HFC-152a	0.119	0.095	0.13	0.097
HFC-161	0.039	0.024	0.03	0.022
HFC-227ca	0.268	0.249	0.31	
HFC-227ea	0.264	0.256	0.30	0.322
HFC-236cb	0.239	0.217	0.23	
HFC-236fa	0.253	0.251	0.28	0.264
HFC-23	0.177	0.171	0.20	0.248
HFC-245cb	0.245		0.26	
HFC-245fa	0.256	0.241	0.25	0.261
HFC-272ca	0.082		0.08	
HFC-32	0.114	0.105	0.13	0.155
HFC-41	0.027	0.023	0.02	
HFE-245fa2	0.387	0.332	0.31	
HCFE-235da2	0.449	0.372	0.38	
HFE-125	0.424	0.407	0.44	
HFE-143a	0.198	0.172	0.27	
HFE-356mf2	0.362			
HFE-7100	0.402	0.347	0.31	
HFE-7200	0.412	0.303	0.30	
i7100	0.374			
n7100	0.465			
i7200	0.338			

Table 3. (continued)

Gas	Radiative Forcing, $\text{W m}^{-2} \text{ppbv}^{-1}$			
	Constant Profile	Lifetime Adjusted	WMO [1999]	Jain et al. [2000]
H-Galden 1040X	1.051	0.987	1.05	
Halon 1211	0.313	0.263	0.30	0.251
Halon 2402	0.329			
Halon 1301	0.318	0.289	0.32	0.273
CF_3SF_5	0.567			
CF_4	0.117	0.116	0.08	0.089 ^b
C_2F_6	0.268	0.266	0.25	
C_3F_8	0.283	0.279	0.26	
C_4F_8	0.318	0.314	0.36	
C_4F_{10}	0.375	0.370	0.33	
$\text{CF}_3\text{CF}_2\text{I}$	0.296		0.26	0.293 ^b
CF_3I	0.275	0.168	0.23	0.268 ^b
CH_2Br_2	0.016	0.011	0.01	0.019 ^b
CHF_2Br	0.166	0.146	0.14	0.174 ^b
CH_3Br	0.007	0.005	0.01	0.007 ^b
$\text{CH}_2\text{ClCH}_2\text{Cl}$	0.021			
CHCl_3	0.136	0.094	0.02	
Acetylene	0.051			
Benzene	0.013			
Cyclohexane	0.004			
Ethane	0.003			
Ethene	0.037			
n-butane	0.004			
n-pentane	0.004			
Propane	0.003			
Propylbenzene	0.021			
Styrene	0.046			
Toluene	0.020			

^aWhere available, these correction factors are applied directly; elsewhere, a correction factor based on an empirical least squares fit to the results of Jain et al. [2000] is applied, using lifetimes given by WMO [1999]. The forcings from WMO [1999] and the lifetime corrected forcings from Jain et al. [2000] are also included where data are available. The reference forcing and lifetime for HFC-245fa are from Ko et al. [1999]. The chemical formulae for the gases are given in Table 2.

^bRadiative forcing for a constant trace gas profile.

latitudinally resolved satellite observations of CFC-11 (which were found to agree with balloonsonde observations) and calculated a forcing only 6% smaller than a constant profile case. For a number of gases common to the Naik et al. [2000] and Jain et al. [2000] studies the impact of model-derived profiles differs markedly for some gases (e.g., the corrections for HCFC-123 are 16% and 27% respectively). A. Jain (personal communication, 2000) reports that results from Jain et al. [2000] should be regarded as the most reliable because of the more detailed approach in that study. For the five gases that Freckleton et al. [1998] and Jain et al. [2000] have in common, two gases have derived corrections which differ by more than 30%.

With these words of caution, the following approach is adopted. For those gases common to this study and that of Jain et al. [2000] we adopt their correction factor for the impact of vertical profile. For nine of the 39 gases of Jain et al. [2000], vertical profiles were not available, and they assumed that these gases have a constant vertical profile, even for gases with short lifetimes. We choose, instead, to adopt a simple correction

factor based on atmospheric lifetime. It is recognized that such a correction factor is best applied using the stratospheric lifetime, because it is this that determines the rate of falloff above the tropopause [see Freckleton et al., 1998; Naik et al., 2000]; indeed, plotting the correction factors of Naik et al. [2000] against stratospheric lifetime yields a tight relationship (see Figure 2). However, for most gases, the stratospheric lifetime is not available. Although less robust, there remains a general relationship between the lifetime and the impact of the vertical profile on the forcing (Figure 2). Using the Jain et al. [2000] results, we have derived an empirical curve fit such that the fractional correction to the forcing for lifetimes greater than 0.25 years is given by $1 - 0.241 t^{-0.358}$, where t is the lifetime in years. For gases of shorter lifetime, we use the minimum value (0.61) in the Jain et al. [2000] study. There is clearly much uncertainty in applying such corrections, and this will be a significant source of error; however, the errors in using these corrections should be lower than the error in applying no correction at all.

After application of these corrections, we believe that

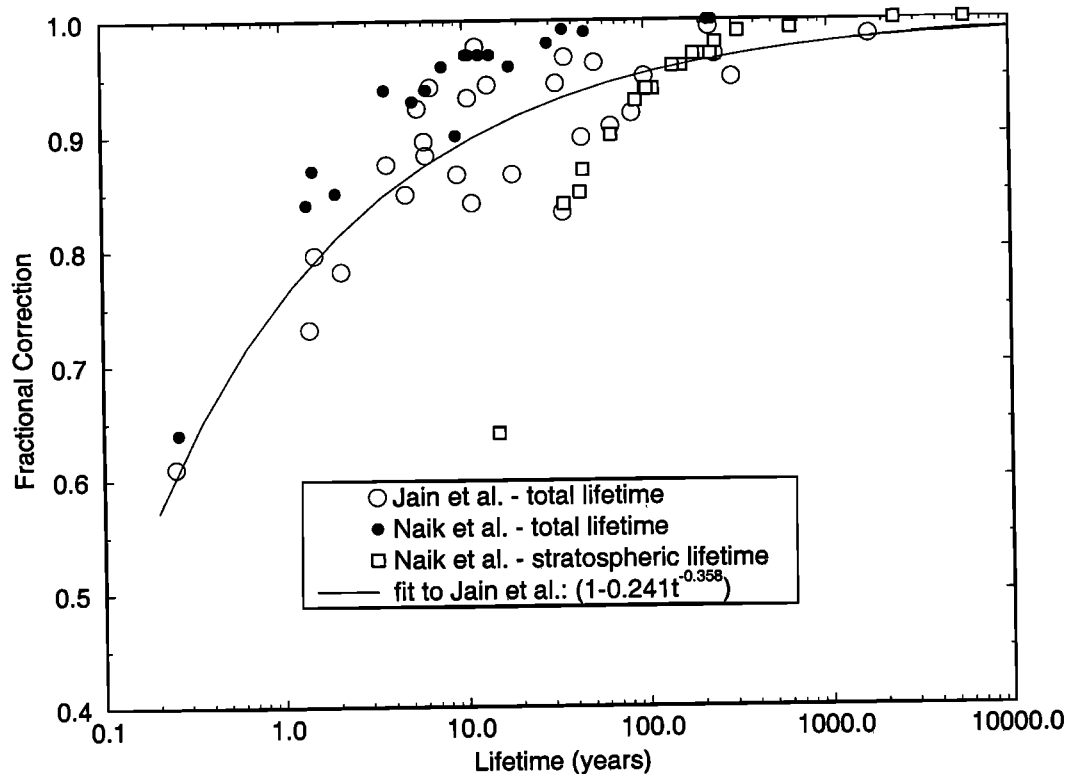


Figure 2. The correction factors required to calculate radiative forcings which account for stratospheric decay from those calculated with a uniform profile are plotted as a function of lifetime. The plot shows an empirical least squares fit to the correction factors from *Jain et al.* [2000] to estimate the factors required for gases where the model-derived vertical profiles are not available.

the uncertainties in the calculated forcings arising from different treatments of the vertical profile of the gases will be comparable to the errors in the spectroscopic measurements, the radiation scheme, and the choice of tropopause (each of the order of 5-10%).

5.2. Results

The global and annual mean forcing values, averaged where more than one cross section was used, are shown in Table 3. These assume that radiative forcing varies linearly with cross section, a valid assumption if temperature-dependent band changes are assumed to be negligible [see *Christidis et al.*, 1997] and the magnitude of errors in the spectra, such as baseline drifts, are frequency independent. The forcings of *Jain et al.* [2000] and *WMO* [1999] have also been included for comparison. HFC-245fa is not included by *WMO* [1999], and so the lifetime and reference forcing of *Ko et al.* [1999] has been used instead. The 100-year global warming potentials (GWPs), computed using our forcings and the *WMO* [1999] lifetimes, are given in Table 4. The radiative forcings show good agreement in general, with 51 of the 65 gases agreeing to within 15% of the *WMO* [1999] values (although it should be noted that some of the *WMO* [1999] values were based on our own earlier work).

For the instantaneous forcings (not shown), the uncalibrated NBM values were found to vary between 98 and 104% of the corresponding FRFM values for all but five gases. These remaining gases, acetylene, benzene, toluene, perfluoromethane, and methyl bromide, all exhibit sharp spectral features and showed deviations of up to 13%. This illustrates that the more approximate model, the NBM, in general performs very well except when the infrared spectrum contains sharply varying spectral features. This “problem” is more likely to be observed when cross-sectional spectra are used for lighter molecules (e.g., acetylene) since for molecular transitions the line spacing is inversely proportional to molecular moments of inertia (hence heavy molecules generally have strongly overlapping lines and less detailed line structure) [see, e.g., *Griffiths and deHaseth*, 1986].

To investigate whether this artifact of the NBM affects the adjusted, cloudy-sky forcings in a consistent manner, we investigate an alternative method of forcing agreement between the FRFM and the NBM. The cross sections of each of the above five gases and CFC-11, representing the “typical” case, were scaled in frequency by the difference in the global-mean forcing spectra of the NBM and FRFM for the instantaneous clear-sky forcing. These effective cross sections were then used in the

Table 4. Global Warming Potentials (GWPs) Relative to CO₂, Calculated Using Lifetimes From *WMO* [1999], the Lifetime-Corrected Forcings of This Study, and a 100-Year Time Horizon^a

Gas	Forcing, W m ⁻² ppbv ⁻¹	Lifetime, years	100-Year GWP
CFC-11	0.242	45	4,500
CFC-12	0.321	100	10,600
HCFC-123	0.141	1.4	80
HCFC-124	0.193	6.1	540
HCFC-141b	0.130	9.2	650
HCFC-142b	0.163	18.5	1,900
HCFC-21	0.140	2	170
HCFC-225ca	0.202	2.1	130
HCFC-225cb	0.280	6.2	540
HCFC-22	0.208	11.8	1,800
HFC-125	0.223	32.6	3,600
HFC-134	0.180	10.6	1,200
HFC-134a	0.159	13.6	1,300
HFC-143	0.118	3.8	340
HFC-143a	0.148	53.5	5,000
HFC-152a	0.095	1.5	140
HFC-161	0.024	0.25	10
HFC-227ca	0.249	32.6	2,900
HFC-227ea	0.256	36.5	3,200
HFC-236cb	0.217	14.6	1,300
HFC-236fa	0.251	226	8,400
HFC-23	0.171	243	13,000
HFC-245fa	0.241	7.6	860
HFC-32	0.105	5.6	710
HFC-41	0.023	3.7	160
HFE-245fa2	0.332	4.4	610
HCFE-235da2	0.372	2.6	330
HFE-125	0.407	165	14,000
HFE-143a	0.172	5.7	620
HFE-7100	0.347	5	440
HFE-7200	0.303	0.77	60
H-Galden 1040X	0.987	48	8,700
Halon 1211	0.263	11	1,100
Halon 1301	0.289	65	6,200
CF ₄	0.116	50000	8,300
C ₂ F ₆	0.266	10000	12,100
C ₃ F ₈	0.279	2600	9,200
C ₄ F ₈	0.314	3200	9,700
C ₄ F ₁₀	0.370	2600	9,600
CF ₃ I	0.168	0.005	<1
CH ₂ Br ₂	0.011	0.41	2
CHF ₂ Br	0.146	7	490
CH ₃ Br	0.005	0.7	2
CHCl ₃	0.094	0.51	30

^aThe lifetime for HFC-245fa is taken from *Ko et al.* [1999], and the chemical formulae for these gases are given in Table 2.

NBM to calculate the adjusted, cloudy-sky forcings, as illustrated in Table 5. The NBM instantaneous, clear-sky forcings using the effective cross sections are in good agreement with the FRFM values, which suggests that the difficulties encountered by band models for sharp spectral signatures can be corrected for in the absorption cross-sectional spectra. These two methods, calibrating the broadband instantaneous (clear-sky) NBM

forcing for each gas to that calculated using the FRFM and then scaling the adjusted (cloudy-sky) forcing, or calculating the adjusted forcing using an effective cross section, are shown to agree to better than 3% in Table 5. This strongly suggests that the differences in forcings between the two models for each gas are unaltered by the inclusion of clouds or stratospheric adjustment.

H-Galden 1040X is the strongest greenhouse gas in this compilation, with a forcing of 0.987 W m⁻² ppbv⁻¹, where 59% of the integrated cross section lies within the 800 to 1200 cm⁻¹ atmospheric “window” and contributes 76% of the forcing. The HFEs and HCFE-235da2 have forcings of the order of 0.4 W m⁻² ppbv⁻¹, which are stronger than the forcing of CFC-11. For the HCFCs, only HCFC-22, HCFC-141b, and HCFC-142b are currently detected in significant quantities in the atmosphere, with HCFC-22 at 122 pptv in 1996, almost half the concentration of CFC-11 and increasing at a rate of 5 pptv yr⁻¹ [*Miller et al.*, 1998]. The radiative forcing of HCFC-22 is 0.208 W m⁻² ppbv⁻¹, approximately 86% of the CFC-11 forcing, but its shorter lifetime of 11.8 years gives it a 100-year GWP, one measure of the integrated radiative effect of the trace gas over its atmospheric lifetime, of 1800 relative to CO₂, compared with 4500 for CFC-11. For the two detectable HFCs in significant quantities (HFC-23 and HFC-134a), HFC-23, with a concentration in 1995 of 11 pptv and increasing at a rate of 5% yr⁻¹ [*Oram et al.*, 1998], is shown to have a forcing of 0.171 W m⁻² and a strong GWP. Consistent with previous results [*Highwood et al.*, 1999], the nonmethane hydrocarbons are found to have very small radiative forcing values in the range 0.003–0.051 W m⁻² ppbv⁻¹. Differences between the forcing values for acetylene, benzene, n-butane, propane, and toluene given in Table 3 and those reported previously by *Highwood et al.* [1999] reflect the improved infrared absorption cross sections used for these species in the present work. Finally, the forcing for CF₃SF₅ is included here for completeness but is the subject of a separate study [*Sturges et al.*, 2000].

Table 6 shows the trace gases which we calculate have forcings that differ from those reported by *WMO* [1999] by more than 15%. HFC-41 also shows a difference but is not included because the forcing, which is small, agrees to the precision (two decimal places) of that reported by *WMO* [1999]. The differences in forcing values for HFC-161, CH₃Br, and CF₃I from those reported by *WMO* [1999] from *Christidis et al.* [1997] are due purely to the different correction factors for stratospheric lifetime. HFC-227ca (*WMO* [1999], taken from *Christidis et al.* [1997]) and HFC-32 (*WMO* [1999], taken from *Pinnock et al.* [1995]) show differences in their integrated cross sections of up to 16%, which is of the correct order for the difference between forcings, assuming the same correction factors. HFC-32 absorbs strongly in the 800 to 1200 cm⁻¹ atmospheric window, and consequently the difference in cross section is likely to have a greater influence on the forcing.

Table 5. Radiative Forcings Calculated Using Measured and Effective Cross Sections for CFC-11 and Gases With Sharp Spectral Signatures^a

Gas	FRFM	Measured Cross Section		Effective Cross Section	
		Adjusted	Adjusted and FRFM Scaled	Instantaneous	Adjusted
CFC-11	0.3283	0.2710	0.2689	0.3283	0.2689
Acetylene	0.0591	0.0466	0.0507	0.0591	0.0511
Benzene	0.0166	0.0138	0.0134	0.0166	0.0130
CF ₄	0.1350	0.1058	0.1168	0.1349	0.1168
CH ₃ Br	0.0078	0.0062	0.0065	0.0077	0.0065

^aThe adjusted forcing refers to the narrowband model (NBM) adjusted, cloudy-sky forcing. For the measured cross section, “scaled” represents the final adjusted forcing after calibration to the FRFM values. The effective cross section is calculated by multiplying the measured cross section by the difference in clear-sky global forcing, as a function of frequency, between the RFM and NBM. In this case the instantaneous and adjusted NBM forcings therefore require no linear scaling calibration, and the difference between columns four and six hence describes the reliability of this method. Values are given in $\text{W m}^{-2} \text{ ppbv}^{-1}$.

Improvements made to the NBM, used in the studies of *Pinnock et al.* [1995], *Christidis et al.* [1997], and this study, will also contribute marginally to the forcing differences. The forcing for HCFC-21 also shows a significant difference from that of *WMO* [1999] from *Christidis et al.* [1997]. In that study a cloudy-sky, adjusted forcing of $0.185 \text{ W m}^{-2} \text{ ppbv}^{-1}$ was calculated for a uniform profile (compared with 0.173 in this study). A lifetime corrected value using the *WMO* [1999] correction would therefore give $0.148 \text{ W m}^{-2} \text{ ppbv}^{-1}$ (compared with 0.140 here) and not $0.17 \text{ W m}^{-2} \text{ ppbv}^{-1}$, as incorrectly tabulated by *WMO* [1999].

Perfluoromethane (CF₄) is a stronger greenhouse gas in this study than reported by *WMO* [1999] from *Myhre and Stordal* [1997], and by *Jain et al.* [2000]. The cross-sectional spectrum of *McDaniel et al.* [1991] used for both of these studies was recorded at a higher resolution than the Ford spectrum, but bands and particularly strong lines in the band centers, at 1283 cm^{-1} , for

example, are much weaker, giving an integrated cross section approximately 73% that of the Ford spectrum. This is due possibly to band saturation, as suggested by *Roehl et al.* [1995]; the integrated cross section of *Roehl et al.* [1995] agrees with that used in this study to within 7%, supporting the value derived here.

The forcing for HFE-143a in this study is 36% lower than that reported by *WMO* [1999], based on the results of *Good et al.* [1998]. The absorption cross section used by *Good et al.* [1998] was simulated from calculated rotational/vibrational frequencies and absolute intensities as discussed by *Good and Francisco* [1998]. The simulated spectrum shows differences in spectral features, which are attributed to convolved or unresolved signatures in the measured spectrum, although the Ford spectrum, at a resolution of 0.06 cm^{-1} , shows identical features. The calculated raw forcing values of *Good et al.* [1998] use simulated spectra, with values varying from 6% (CFC-12) to 39% (HFC-134) stronger than

Table 6. Gases for Which the Global Mean Radiative Forcing Calculated Here Differs From Those Reported by *WMO* [1999] by More Than 15%^a

Gas	Forcing, $\text{W m}^{-2} \text{ ppbv}^{-1}$			Reference
	This Study	<i>WMO</i> [1999]	Percentage Difference	
HCFC-21	0.140	0.17	-17.4	<i>Christidis et al.</i> [1997]
HCFC-123	0.141	0.20	-29.7	<i>Fisher et al.</i> [1990]
HCFC-142b	0.163	0.20	-18.4	<i>Fisher et al.</i> [1990]
HCFC-225ca	0.202	0.27	-25.1	
HFC-32	0.105	0.13	-19.2	<i>Pinnock et al.</i> [1995]
HFC-134a	0.159	0.19	-16.6	<i>Fisher et al.</i> [1990]
HFC-152a	0.095	0.13	-26.9	
HFC-161	0.024	0.03	-20.9	<i>Christidis et al.</i> [1997]
HFC-227ca	0.249	0.31	-19.6	<i>Christidis et al.</i> [1997]
CHCl ₃	0.094	0.02	+370	
CH ₃ Br	0.005	0.01	-52.8	<i>Christidis et al.</i> [1997]
CF ₃ I	0.168	0.23	-27.0	<i>Christidis et al.</i> [1997]
CF ₄	0.116	0.08	+46.3	<i>Myhre and Stordal</i> [1997]
HFE-143a	0.172	0.27	-36.2	<i>Good et al.</i> [1998]

^aThe source of the *WMO* [1999] data, where available, is indicated.

those reported by *WMO* [1999]. It is therefore not inconsistent with the overestimated forcing of HFE-143a, as observed here.

The remaining gases of *WMO* [1999] are based either on the results of *Fisher et al.* [1990] or on "grey" literature where no comparison is possible. In particular, the large difference in forcing for trichloromethane cannot be accounted for, since the *WMO* [1999] value was not based on a published estimate. The calculations by *Fisher et al.* [1990] are based on a radiative-convective model with broader spectral bands compared with those used here. Furthermore, a differing tropopause height definition can also affect the forcing value by up to 9% [e.g., *Freckleton et al.*, 1998], while differing absorption cross sections have been shown to produce errors of a similar magnitude. Different vertical profiles in the reference profile and spectroscopic data also combine as second-order effects to enhance this difference. It is impossible to quantify exactly the contribution of these effects to the differences observed between the two studies given that this information was not published. A further nine trace gases (HCFC-124, HCFC-225cb, HFC-23, HFC-227ea, HFC-236fa, C₄F₈, C₄F₁₀, HFE-7100 and halon-1211) show radiative forcing differences from *WMO* [1999] of 10–15%. These forcings are based mainly on the results of *Fisher et al.* [1990], on grey literature, or on calculations using simple models. Errors of this magnitude are typically attributable to any of the factors mentioned previously and are therefore harder to assess given the lack of information. The radiative forcings for these gases, and indeed all of the gases reported here, have been calculated in a consistent manner and hence are easier to compare relative to a fixed forcing, such as CFC-11, if desired.

Our values can be compared with the comprehensive study of *Jain et al.* [2000], most directly by comparing the constant profile cases in both studies. In general, the agreement is excellent. Of the 26 gases common to both studies, 11 agree to better than 5%, while a further 6 agree to within 10%. However, in addition to CF₄ which was discussed above, the *Jain et al.* [2000] values for four gases are much higher than ours. These are HFC-134a (23% higher), HFC-227ea (24%), HFC-23 (34%), and HFC-32 (35%); by coincidence, this list includes the two most abundant HFCs in the atmosphere: HFC-134a and HFC-23.

We are unable to fully explain these discrepancies. Differences in the absorption cross section can explain about half the discrepancy for HFC-23 and one third that for HFC-32 but very little for the other two gases. The narrowband and line-by-line results agree well for these gases, and our narrowband model is similar to that used by *Jain et al.* [2000]. It will probably be necessary to do a tight intercomparison of the two sets of work to resolve the cause of these differences.

6. Conclusions

Cloudy-sky, adjusted radiative forcings for 65 halocarbons and nonmethane hydrocarbons have been calculated using a narrowband model and the FRFM line-by-line code. The FRFM was compared with other line-by-line radiation codes and found to agree in irradiance to better than 1.5% and in CO₂ forcing to better than 1.0%. The FRFM was further validated against observations using the ARIES instrument and found to agree to better than 1.8% in frequency-integrated radiance. Both models were used to calculate the radiative forcings, using absorption cross sections measured principally at the Ford Motor Company. The radiative forcings for 11 of the gases, including four isomers, have, to the author's knowledge, not been published previously. The adjusted, cloudy-sky radiative forcings are in good agreement with *WMO* [1999] values for 51 gases, while 14 gases show differences greater than 15%. The agreement between our results and those of *Jain et al.* [2000], for the 26 gases in common, is generally excellent, although four gases were found to differ by more than 20%.

The combination of the use of a validated line-by-line code, the reassessment of the infrared spectra, and the use of a single methodology for all gases suggests that the forcings presented here are a general improvement over *WMO* [1999]. The 65-molecule data set reported here is the most comprehensive and consistent database yet available to evaluate the relative impact of halocarbons and nonmethane hydrocarbons on climate change. There remains a need to compare absorption spectra, radiative forcing values, and the impact of vertical profiles on the forcing. The work presented here will contribute to such comparisons.

Acknowledgments. The work was funded by the Department of the Environment, Transport and the Regions under contract EPG/1/1/73. We thank A. Dudhia for providing and supporting the RFM, J. P. Taylor for the provision of ARIES data and E. J. Highwood for her help with the SWAGG spectra and comments. We are grateful to two referees for many pertinent comments and to A. Jain for clarifying some aspects of his calculations.

References

- Christidis, N., M. Hurley, S. Pinnock, K. Shine, and T. Wallington, Radiative forcing of climate change by CFC-11 and possible CFC replacements, *J. Geophys. Res.*, **102**, 19,597–19,609, 1997.
- Clerbaux, C., R. Colin, P. Simon, and C. Granier, Infrared cross sections and global warming potentials of 10 alternative hydrohalocarbons, *J. Geophys. Res.*, **98**, 10,491–10,497, 1993.
- Clough, S., M. Iacono, and J.-L. Moncet, Line-by-line calculations of atmospheric fluxes and cooling rates: Application to water vapor, *J. Geophys. Res.*, **97**, 15,761–15,785, 1992.
- Dudhia, A., RFM v3 software user's manual, technical report, *ESA Doc. PO-MA-OXF-GS-0003*, Dep. of Atmos.,

- Oceanic and Planet. Phys., Univ. of Oxford, Oxford, England, 1997.
- Edwards, D., GENLIN2: The new Oxford line-by-line atmospheric transmittance/radiance model: Description and user's guide, technical report, *Intern. Memo. 87.2*, Dep. of Atmos., Oceanic and Planet. Phys., Univ. of Oxford, Oxford, England, 1987.
- Ellingson, R., J. Ellis, and S. Fels, The intercomparison of radiation codes used in climate models: Long wave results, *J. Geophys. Res.*, *96*, 8929–8953, 1991.
- Fisher, D., C. Hales, W.-C. Wang, M. Ko, and N. Sze, Model calculations of the relative effects of CFCs and their replacements on global warming, *Nature*, *344*, 513–516, 1990.
- Freckleton, R., E. Highwood, K. Shine, O. Wild, K. Law, and M. Sanderson, Greenhouse gas radiative forcing: Effects of averaging and inhomogeneities in trace gas distribution, *Q. J. R. Meteorol. Soc.*, *124*, 2099–2127, 1998.
- Good, D., and J. Francisco, Structure and vibrational spectra of chlorofluorocarbon substitutes: An experimental and ab initio study of fluorinated ethers CHF₂OCF₃ (E125), CHF₂OCHF₂ (E134) and CH₃OCF₃ (E143a), *J. Phys. Chem. A*, *102*, 1854–1864, 1998.
- Good, D., J. Francisco, A. Jain, and D. Wuebbles, Lifetimes and global potentials for dimethyl ethers and for fluorinated ethers: CH₃OCF₃ (E143a), CHF₂OCHF₂ (E134), CHF₂OCF₃ (E125), *J. Geophys. Res.*, *103*, 28,181–28,186, 1998.
- Griffiths, P., and J. deHaseth, *Fourier Transform Infrared Spectrometry*, vol. 83, Wiley-Interscience, New York, 1986.
- Hansen, J., M. Sato, and R. Ruedy, Radiative forcing and climate responses, *J. Geophys. Res.*, *102*, 6831–6864, 1997.
- Heathfield, A., C. Anastasi, A. McCulloch, and F. Nicolaisen, Integrated infrared absorption coefficients of several partially fluorinated ether compounds: CF₃OCF₂H, CF₂HOCF₂H, CH₃OCF₂CF₂H, CH₃OCF₂CFClH, CH₃CH₂OCF₂CF₂H, CF₃CH₂OCF₂CF₂H and CH₂=CHCH₂OCF₂CF₂H, *Atmos. Environ.*, *32*, 2825–2833, 1998.
- Highwood, E., and K. Shine, Radiative forcing and global warming potentials of 11 halogenated compounds, *J. Quant. Spectrosc. Radiat. Transfer*, *66*, 169–183, 2000.
- Highwood, E., K. Shine, M. Hurley, and T. Wallington, Estimation of direct radiative forcing due to non-methane hydrocarbons, *Atmos. Environ.*, *33*, 759–767, 1999.
- Imasu, R., A. Suga, and T. Matsuno, Radiative effects and halocarbon global warming potentials of replacement compounds for chlorofluorocarbons, *J. Meteorol. Soc. Jpn.*, *73*, 1123–1136, 1995.
- Intergovernmental Panel on Climate Change (IPCC), 1994: *Radiative Forcing of Climate Change*, Cambridge Univ. Press, New York, 1995.
- Jain, A., B. Briegleb, K. Minschwaner, and D. Wuebbles, Radiative forcings and global warming potentials of 39 greenhouse gases, *J. Geophys. Res.*, *105*, 20,773–20,790, 2000.
- Kalman, R., A new approach to linear filtering and prediction problems, *Trans. ASME, Ser. D, J. Basic Eng.*, *82*, 35–45, 1960.
- Ko, M., R.-L. Shia, N.-D. Sze, H. Magid, and R. Bray, Atmospheric lifetime and global warming potential of HFC-245fa, *J. Geophys. Res.*, *104*, 8173–8181, 1999.
- Malkmus, W., Random Lorentz band model with exponential-tailed S^{-1} line-intensity distribution function, *J. Opt. Soc. Am.*, *57*, 323–329, 1967.
- McDaniel, A., C. Cantrell, J. Davidson, R. Shetter, and J. Calvert, The temperature dependent, infrared absorption cross-sections for the chlorofluorocarbons: CFC-11, CFC-12, CFC-13, CFC-14, CFC-22, CFC-113, CFC-114, CFC-115, *J. Atmos. Chem.*, *12*, 211–227, 1991.
- Miller, B., J. Huang, R. Weiss, R. Prinn, and P. Fraser, Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, *J. Geophys. Res.*, *103*, 13,237–13,248, 1998.
- Myhre, G., and F. Stordal, Role of spatial and temporal variations in the computation of radiative forcing and GWP, *J. Geophys. Res.*, *102*, 11,181–11,200, 1997.
- Myhre, G., E. Highwood, K. Shine, and F. Stordal, New estimates of radiative forcing due to well-mixed greenhouse gases, *Geophys. Res. Lett.*, *25*, 2715–2718, 1998.
- Naik, V., A. Jain, K. Patten, and D. Wuebbles, Consistent sets of atmospheric lifetimes and radiative forcings on climate for CFC replacements: HCFCs and HFCs, *J. Geophys. Res.*, *105*, 6903–6914, 2000.
- Oram, D., W. Sturges, S. Penkett, A. McCulloch, and P. Fraser, Growth of fluoroform (CHF₃, HFC-23) in the background atmosphere, *Geophys. Res. Lett.*, *25*, 35–38, 1998.
- Pinnock, S., and K. Shine, The effects of changes in HITRAN and uncertainties in the spectroscopy on infrared irradiance calculations, *J. Atmos. Sci.*, *55*, 1950–1964, 1998.
- Pinnock, S., M. Hurley, K. Shine, T. Wallington, and T. Smyth, Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons, *J. Geophys. Res.*, *100*, 23,227–23,238, 1995.
- Roehl, C., D. Boglu, C. Bruhl, and G. Moortgat, Infrared band intensities and global warming potentials of CF₄, C₂F₆, C₃F₈, C₄F₁₀, C₅F₁₂, C₆F₁₄, *Geophys. Res. Lett.*, *22*, 815–818, 1995.
- Rothman, L., et al., The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 edition, *J. Quant. Spectrosc. Radiat. Transfer*, *60*, 665–710, 1998.
- Shine, K., On the cause of the relative greenhouse strength of gases such as the halocarbons, *J. Atmos. Sci.*, *48*, 1513–1518, 1991.
- Sihra, K., Laboratory measurements of near-infrared methane bands for remote sensing of the Jovian atmosphere, Ph.D. thesis, Univ. of Oxford, Oxford, England, 1998.
- Sturges, W., T. Wallington, M. Hurley, K. Shine, K. Sihra, A. Engel, D. Oram, S. Penkett, R. Mulvaney, and C. Brenninkmeijer, A potent new greenhouse gas identified in the atmosphere: SF₅CF₃, *Science*, *289*, 611–613, 2000.
- Varanasi, P., and V. Nemtchinov, Thermal infrared absorption coefficients of CFC-12 at atmospheric conditions, *J. Quant. Spectrosc. Radiat. Transfer*, *51*, 679–687, 1994.
- Wiscombe, W., Extension of the doubling method to inhomogeneous sources, *J. Quant. Spectrosc. Radiat. Transfer*, *16*, 477–489, 1976.
- World Meteorological Organization (WMO), Atmospheric ozone 1985, vol. I, *Rep. 16*, Geneva, 1986.
- World Meteorological Organization (WMO), Scientific assessment of ozone depletion: 1998, *Rep. 44*, Global Ozone Res. and Monit. Project, Geneva, 1999.
- M.D. Hurley and T.J. Wallington, Mail Drop SRL 3083, Ford Motor Company, Dearborn, MI 48121-2053. (e-mail: mhurley3@ford.com)
- K.P. Shine and K. Sihra, Department of Meteorology, University of Reading, Earley Gate, PO Box 243, Reading, RG6 6BB, England, UK. (e-mail: K.P.Shine@reading.ac.uk)

(Received April 14, 2000; revised August 16, 2000; accepted October 5, 2000.)