Radiative Effects and Halocarbon Global Warming Potentials
of Replacement Compounds for Chlorofluorocarbons

By Ryoichi Imasu
National Institute for Resources and Environment, Tsukuba, Ibaraki 305, Japan

Atsuo Suga
Research Institute of Innovative Technology for the Earth, Tsukuba, Ibaraki 305, Japan

and

Taroh Matsuno
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, Hokkaido 060, Japan

(Manuscript received 15 June 1995, in revised form 16 October 1995)

Abstract

Instantaneous radiative forcing was calculated for 5 fluoroalcohols, 21 fluoroethers, and 5 fluoroamines which had been proposed as the replacement compounds for the currently used chlorofluorocarbons (CFCs) in refrigeration. The atmospheric lifetimes of the compounds were also estimated from highest-occupied molecular orbital (HOMO) energy. Based on the radiative forcing and atmospheric lifetimes, halocarbon global warming potentials (HGWP) were evaluated for the replacement compounds. Most of the HGWP values were smaller than 0.1 owing to their shorter lifetimes, and the results indicate that these compounds could be valid candidates as replacements for currently used CFCs from the point of view of HGWP.

The spectral cooling rate profiles were calculated for the replacement compounds in order to study the vertical structure of their radiative effects. It was found that overlapping of the absorption bands of a compound with those of ozone causes a significant cooling in the stratosphere, even if the compound does not exist in the stratosphere. This cooling does not directly relate to the HGWP value and the cooling rate profile in the troposphere. Therefore, it can be said that the vertical structure of the radiative effects caused by the compounds should be taken into consideration as well as HGWP or GWP values when we assess the environmental effects due to replacement compounds. In this study, one parameter, defined as the ratio of the cooling rate at 30 km and the tropopause, was proposed as a measure of the cooling in the stratosphere.

Spectral-resolution dependency of the calculated radiative effects was also studied. The results show that the resolution should be finer than about 50 cm\(^{-1}\) to calculate the radiative forcing and cooling rate precisely.

1. Introduction

Since Molina and Rowland (1974) and Stolarski and Cicerone (1974) pointed out that chlorofluorocarbons (CFCs) are responsible for the stratospheric ozone depression, great efforts for developing their replacement compounds which do not disturb the ozone layer have been expended. However, most of the replacements are recognized to be greenhouse gases because they have strong infrared absorption bands in the atmospheric window region, much as CFCs have. Therefore, it can be said that the global warming potential (GWP) of the compounds is one of the important criteria for selecting the valid candidates as replacements to CFCs.

Generally, the global warming potential is defined as the time-integrated commitment to the radiative forcing (which is defined as the net radiation flux change at the tropopause) or the surface temperature change from an instantaneous release of
the gas into the atmosphere (e.g., Hansen et al., 1989), and is usually expressed as a relative value to that of a reference gas such as CO$_2$ or CFC11 (Fisher et al., 1990; IPCC, 1994). Since the radiative forcing is a function of not only the infrared absorption strength of the chemical compound considered but also the degree of overlap effects of absorption bands with other atmospheric constituents, radiative transfer calculations using an atmospheric model are necessary to evaluate the radiative forcing. As can easily be seen from the definition, the other dominant factors which determine the GWP is the atmospheric concentration of the compound, which can be correspond to the lifetime of the compound in the atmosphere. According to this definition, GWPs have been estimated for some CFCs, HCFCs, and HFCs using radiative-convective photochemical models (e.g., Fisher et al., 1990; Shi, 1992; Daniel, 1995).

As a joint research between Research Institute of Innovative Technology for the Earth (RITE) and National Institute for Resources and Environment (NIRE), we have studied the radiative effects of the chemical compounds which have been proposed as the replacements for the currently used CFCs in refrigeration. In this paper, we report the radiative forcing, lifetimes, and halocarbon global warming potentials (HGWP: GWPs relative to CFC-11) for 5 fluoroalcohols, 21 fluoroethers, and 5 fluoroamines. These properties were estimated on the basis of the experimentally measured infrared data and the quasi-theoretically derived rate constants for the reaction between the compounds and the OH radical. In addition, we also report the results of the vertical structure analysis for the radiative effects of the compounds.

2. Calculations

2.1 Absorption cross section

The replacement compounds studied are listed in Table 1 with their chemical formulas. One of the most fundamental properties for estimating GWP (or HGWP) of a compound is its infrared absorption cross section. In this study, we calculated the cross sections of the compounds based on the transmittance data measured by Suga et al. (1994) using an FT-IR spectrometer with a 10 cm-long cell at 296 K and 1.5 mmHg. The wavenumber resolution of the measurement is 0.96449 cm$^{-1}$ after apodization. Because of the instability of the instrument, such as drifting of the detector sensitivity, most of the measured transmittances were biased and their base lines should be corrected before being converted into cross sections. As the baseline correction, we adopted a procedure that all the raw transmittances were scaled so that the average of the transmittance in the spectral region from 2600 to 2700 cm$^{-1}$, where no significant absorption bands exist, became unity.

2.2 Radiation flux and forcing

The monochromatic upward ($F_{\uparrow}^\nu$) and downward ($F_{\downarrow}^\nu$) fluxes are given by (Liou, 1980),

$$F_{\downarrow}^\nu(\tau) = 2\pi B^\nu(T_s)E_3(\tau_1 - \tau) + 2\int_\tau^{\tau_1} \pi B^\nu[T(\tau')]E_2(\tau' - \tau) d\tau'$$

(1)

$$F_{\downarrow}^\nu(\tau) = 2\int_0^{\tau_1} \pi B^\nu[T(\tau')]E_2(\tau' - \tau) d\tau'$$

(2)

$$E_n(\tau) = \int_1^\infty e^{-\tau x} x^n dx$$

(3)

where $\tau$ is the optical depth from the top of the atmosphere to a height $Z$, $T$ is atmospheric temperature, $T_s$ is the surface temperature, and $B(T)$ is the Planck function. The total radiation fluxes $F^\uparrow$ and $F^\downarrow$ can be evaluated by integrating the monochromatic fluxes over the whole spectral range. In this study, the integration was carried out over a range from 700 to 1500 cm$^{-1}$ where most of the absorption bands of the replacement compounds exist. The instantaneous radiative forcing $RF_x$ due to a compound $x$ is defined as the net flux change ($F^\uparrow - F^\downarrow$) at the tropopause height.

The spectral cooling rate of the atmosphere ($dT/dt$)$_\nu$, which has been recently used to study the atmospheric radiation field by Clough et al. (1992), is calculated by

$$\left(\frac{dT}{dt}\right)_\nu = -\frac{1}{C_p \rho} \frac{\Delta F^\nu}{\Delta z}$$

(4)

$$\Delta F^\nu = F^\nu(z + \Delta z) - F^\nu(z)$$

(5)

$$F^\nu(z) = F^\nu_{x1}(z) - F^\nu_{xj}(z)$$

(6)

where $C_p$ and $\rho$ are the specific heat at constant pressure and the air density, respectively. By integrating the spectral cooling rate over the whole spectral range, the total cooling rate $dT/dt$ of the atmosphere can be evaluated.

The optical depth of each atmospheric layer which contains no replacement compounds was calculated by a line-by-line calculation program FASCODE 3P (Clough et al., 1985, 1989) for 6 types of model atmosphere (TPL: tropical, MLS: mid-latitude summer, MLW: mid-latitude winter, SAS: sub-arctic summer, SAW: sub-arctic winter, and USS: the U.S. standard) using the HITRAN 92 database (Rothman et al., 1992). The atmospheric constituents considered in the calculation were N$_2$, O$_2$, H$_2$O, CO$_2$, O$_3$, CH$_4$, N$_2$O, CO. In our calculations, a clear sky condition was assumed. However, this assumption was different from that of Fisher et al. (1990) in which 50% of cloud coverage was assumed. The vertical profiles of temperature in the model atmospheres and concentration profiles of the constituents are shown in Figs. 1a and 1b, respectively.
| Compound | Chemical formula | Molecular weight (g/mol) | Integrated cross-section (10^{-16} cm/molecule) | RF_x (10^{-5} W/cm²) | RF_x relative to CFC-11 (Mol Basis) | RF_x relative to CFC-11 (Weight Basis) | Net flux change at the surface (10^{-5} W/cm²) | Cooling rate ratio (30 km/tropo.) |
|----------|------------------|--------------------------|-----------------------------------------------|----------------------|-------------------------------------|----------------------------------------|-------------------------------------------|-----------------------------------|
| CFC-11   | CFCl_3           | 137.3                    | 0.978                                         | -3.47                | 1.00                                | 1.00                                   | -2.68                                     | -0.25                             |
| MCF      | CH_2CCCl_2       | 133.4                    | 0.502                                         | -0.780               | 0.225                               | 0.231                                  | -1.29                                     | -0.29                             |
| HFC-125  | CF_3CHF          | 120.0                    | 1.70                                          | -3.08                | 0.888                               | 1.02                                   | -1.91                                     | -0.247                            |
| HFC-134a | CF_3CH_2F        | 102.0                    | 1.35                                          | -2.42                | 0.656                               | 0.884                                  | -1.56                                     | -0.344                            |
| HCFC-141b| CH_2CCCl_2       | 117.0                    | 0.827                                         | -2.18                | 0.628                               | 0.737                                  | -1.55                                     | -0.529                            |
| HCFC-225c| CClF_2CF_2CHClF  | 202.9                    | 1.66                                          | -4.15                | 1.19                                | 0.809                                  | -3.00                                     | -0.405                            |
| E-134    | CHF_2-O-CHF_2    | 118.0                    | 2.55                                          | -5.92                | 1.70                                | 1.99                                   | -4.51                                     | -0.689                            |
| [fluoralcohols] |              |                          |                                               |                      |                                     |                                        |                                           |                                   |
| a1       | (CF_3)_2COH      | 236.0                    | 3.74                                          | -4.49                | 1.29                                | 0.753                                  | -2.81                                     | -0.41                             |
| a3       | (CF_3)_2CH(OH)   | 230.1                    | 2.11                                          | -4.11                | 1.18                                | 0.707                                  | -3.04                                     | -1.12                             |
| a11      | CF_3CH_2OH       | 100.0                    | 1.43                                          | -2.54                | 0.732                               | 1.01                                   | -1.80                                     | -0.40                             |
| a21      | CF_3CF_2CH_2OH   | 150.0                    | 1.79                                          | -3.36                | 0.968                               | 0.886                                  | -2.20                                     | -0.62                             |
| a31      | (CF_3)_2CHOH     | 168.0                    | 2.54                                          | -3.93                | 1.13                                | 0.926                                  | -2.46                                     | -0.31                             |
| [fluoroethers] |              |                          |                                               |                      |                                     |                                        |                                           |                                   |
| me04     | CF_3CF_2-O-CH_3  | 150.0                    | 2.46                                          | -4.46                | 1.29                                | 1.18                                   | -2.92                                     | -0.43                             |
| me08     | CF_3CF_2-O-CH_3  | 132.1                    | 1.91                                          | -3.80                | 1.10                                | 1.14                                   | -2.71                                     | -0.63                             |
| me09     | CF_3CHF-O-CHF_2  | 186.0                    | 3.69                                          | -5.58                | 1.61                                | 1.19                                   | -3.21                                     | -0.22                             |
| me10     | CF_3CHF-O-CHF_2  | 168.0                    | 2.99                                          | -6.09                | 1.76                                | 1.43                                   | -4.25                                     | -0.49                             |
| me17     | CF_3CH_2-O-CHF_2 | 168.0                    | 3.35                                          | -4.72                | 1.56                                | 1.11                                   | -2.75                                     | -0.16                             |
| me18     | CF_3CH_2-O-CHF_2 | 150.0                    | 2.63                                          | -4.99                | 1.44                                | 1.32                                   | -3.53                                     | -0.64                             |
| me20     | CF_3CH_2-O-CH_3  | 114.1                    | 1.52                                          | -2.76                | 0.795                               | 0.957                                  | -1.95                                     | -0.41                             |
| me29     | CF_3CH_2-O-CHF_2 | 150.0                    | 2.79                                          | -4.14                | 1.19                                | 1.09                                   | -2.68                                     | -0.38                             |
| ee02     | CF_3CF_2-O-CHF_2 | 236.0                    | 3.92                                          | -6.79                | 1.96                                | 1.13                                   | -4.30                                     | -0.32                             |
| ee11     | CF_3CF_2-O-CH_3  | 218.0                    | 3.47                                          | -5.86                | 1.69                                | 1.06                                   | -3.70                                     | -0.34                             |
| ee29     | CF_3CF_2-O-CHF_2 | 200.1                    | 3.02                                          | -5.65                | 1.63                                | 1.12                                   | -3.83                                     | -0.48                             |
| ee30     | CHF_2CF_2-O-CH_3 | 182.1                    | 2.49                                          | -5.13                | 1.48                                | 1.11                                   | -3.73                                     | -0.56                             |
| ee68     | CHF_2CF_2-O-CHF_2 | 146.1                   | 2.07                                          | -4.11                | 1.18                                | 1.11                                   | -2.90                                     | -0.61                             |
| mp04     | CF_3CF_2-O-CH_3  | 200.1                    | 2.95                                          | -4.65                | 1.34                                | 0.919                                  | -3.05                                     | -1.04                             |
| mp08     | CHF_2CF_2-O-CHF_2 | 182.1                   | 2.34                                          | -4.48                | 1.29                                | 0.973                                  | -3.2                                      | -0.85                             |
| mp12     | CF_3CHFCF_2-O-CH_3 | 182.1             | 2.58                                          | -4.17                | 1.20                                | 0.906                                  | -2.77                                     | -0.67                             |
| mp32     | CF_3CF_2-O-CH_3  | 164.1                    | 1.96                                          | -3.75                | 1.08                                | 0.904                                  | -2.48                                     | -0.45                             |
| mp54     | CHF_2CF_2-O-CHF_2 | 182.1                   | 2.48                                          | -5.43                | 1.56                                | 1.18                                   | -4.08                                     | -0.71                             |
| mp04     | (CF_3)_2CH-O-CHF | 200.1                    | 2.86                                          | -4.29                | 1.24                                | 0.848                                  | -2.65                                     | -0.94                             |
| mp10     | (CF_3)_2CH-O-CHF | 218.0                    | 3.54                                          | -5.72                | 1.65                                | 1.04                                   | -3.75                                     | -0.44                             |
| mp12     | (CF_3)_2CH-O-CH_3 | 182.1                   | 2.57                                          | -4.10                | 1.18                                | 0.891                                  | -2.61                                     | -0.35                             |
| [fluoroamines] |            |                          |                                               |                      |                                     |                                        |                                           |                                   |
| n34      | (CF_3)_2NCH_3    | 167.1                    | 3.34                                          | -4.48                | 1.29                                | 1.06                                   | -2.98                                     | -0.35                             |
| n42      | (CF_3)_2NCF_2CHF_2 | 253.0          | 4.73                                          | -6.29                | 1.81                                | 0.984                                  | -3.89                                     | -0.44                             |
| n43      | (CF_3)_2NCH_2CF_3 | 235.0                    | 4.29                                          | -5.75                | 1.66                                | 0.968                                  | -3.61                                     | -0.27                             |
| n44      | (CF_3)_2NCHFCF_3 | 253.0                    | 4.70                                          | -5.78                | 1.67                                | 0.904                                  | -3.41                                     | -0.30                             |
| n47      | (CF_3)_2NCH_2CH_3 | 181.1                    | 3.13                                          | -3.98                | 1.15                                | 0.870                                  | -2.60                                     | -0.33                             |
For all model atmospheres, the ground surface temperature is assumed to be the same value as the atmosphere adjacent to the surface. We studied the spectral resolution dependency of the calculated radiative effects. In the calculations, the resolution was changed by averaging the transmittance data obtained at the finest resolution (FASCODE 3P’s resolution).

Generally, the vertical concentration profiles of the replacement compounds are considered to take different features from those of fully halogenated carbons for which the only degradation process is ultraviolet photolysis in the stratosphere, because they can be degraded through other processes such as reactions with the hydroxyl radical and removal in water. However, as their degradation processes, especially dissolution and removal in water, had not been clarified well, the concentration profile of the compounds was assumed to be a very simple one which is similar to that of CFCs, namely it is uniformly 1 ppbv in the troposphere and decreases linearly with altitude up to 24 km, as shown in Fig. 1a.

2.3 Atmospheric lifetime and halocarbon global warming potentials

The only degradation process of the replacement compounds was assumed to be the reaction with OH radical in the atmosphere. The rate constants $k_x$ for the reaction were estimated based on the Highest Occupied Molecular Orbital (HOMO) energies by Suga et al. (1993). Details of the calculations were described in the paper. The lifetime $\tau_x$ of a compound $x$ in the atmosphere is evaluated as

$$\tau_x = \tau_{MCF} \times k_{MCF}/k_x,$$

where $\tau_{MCF}$ is the lifetime of methyl chloroform ($\text{CH}_3\text{CCl}_3$, hereafter, it is abbreviated as MCF) and assumed to be 5.8 years (Ko, personal communication). Discussion on the lifetime of MCF will be made in Section 4. $k_{MCF}$ is the reaction rate constant for MCF which can be expressed in Arrhenius form (De More et al., 1994) as

$$k_{MCF} = 1.8 \times 10^{-12} \exp(-1550.0/T).$$

Generally, the atmospheric mean temperature used in this type of calculation has been recommended to be 277 K (e.g., Prather and Spivakovsky, 1990). However, the temperature was assumed to be 296 K in this study because the calculation of HOMO energies and the measurement of the absorption cross sections were carried out at 296 K. The difference in the lifetimes caused by the temperature difference will be also discussed in Section 4.

The halocarbon global warming potential HGWP which represents the relative warming potential to CFC-11 is defined as

$$\text{HGWP} = \text{GWP}_x/\text{GWP}_{\text{CFC-11}} = (RF_x \times \tau_x)/(RF_{\text{CFC-11}} \times \tau_{\text{CFC-11}}),$$

where $RF_x$ and $RF_{\text{CFC-11}}$ are radiative forcing of the compound and CFC-11, respectively, and $\tau_{\text{CFC-11}}$ is the lifetime of CFC-11 and is assumed to be 60 years (WMO, 1989).
2.4 Errors

The main error sources in estimating the HGWP of the replacement compounds were the measurement error of the infrared absorption cross sections and the estimation error of the rate constants for the reactions with OH radical.

Although the standard deviation (1σ) of our measurements of the absorption cross sections was less than 3% (Suga et al., 1994), the measurement error might be larger because of the systematic errors of our instruments. However, it is generally very difficult to estimate the systematic errors in measuring the radiation spectra with a spectrometer. Hence it is important to compare the measured data with those previously reported for the same compounds. We describe the intercomparisons made for some compounds in Section 3.7. The error in the radiative forcing is owing to that in the cross section data, and the proportionality between them can be assumed unless the feature of the overlapping of absorption bands with other constituents does not change.

On the other hand, the error in estimating the reaction rate constants based on HOMO energy were relatively very large at the present time. The uncertainty of the estimation was about factor 3 in the worst case (Suga et al., 1993), and it dominated the
total error in estimating HGWP. Consequently, the error in the HGWP were of the order of factor 5.

3. Results

3.1 Optical properties

Figure 2 shows the absorption bands of the replacement compounds and the atmospheric transmittance for the mid-latitude summer atmosphere. Comparing these figures, it is easy to see that most of the strong absorption bands of the replacement compounds are located in the atmospheric window.

The integrated absorption cross sections of the compounds are listed in the fourth column of Table 1, where units of the data are cm molecule$^{-1}$, and they can be converted into atm$^{-1}$ cm$^{-2}$ STP by multiplying a value of $2.69 \times 10^{19}$. The results show that all of the cross sections are more than 1.46 times larger than that of CFC-11.

3.2 Radiative forcing

The instantaneous radiative forcing $RF_x$ calculated for the compounds is summarized in Table 1. The model atmosphere used for the calculation is the mid-latitude summer atmosphere. In the sixth and seventh columns of the table, their relative values to that of CFC-11 on a mol and weight basis are also shown, respectively. As can be seen from the results, most of the radiative forcings are larger than that of CFC-11. However, the ratios of the forcing to CFC-11 are smaller than those of the integrated absorption cross sections. Furthermore, the forcings are smaller than that of CFC-11 for some compounds, in spite of their larger absorption strength. These facts clearly show that the radiative forcing is not determined only by the absorption strength but also the degree of overlapping effects of absorption bands with other atmospheric constituents, as mentioned in Section 1. The absolute values of the radiative forcings calculated in this study were almost two times larger than those from Fisher et al. (1990). This difference could be considered to result from that in the cloud assumptions between the models.

Generally, the absolute values of the radiative forcings are dependent on the type of the model atmosphere used for the calculations, as shown in Table 2. However, their relative values to that of CFC-11 (data in parentheses in Table 2) vary little with changing the type of atmosphere. Furthermore, some additional calculations carried out changing the concentration of the compounds show that the radiative forcings are, on average, proportional to the concentrations in the troposphere, whereas their relative values to CFC-11 do not vary with the concentration changes. Also shown in Table 1 are the net flux changes at the surface, which can be a measure of the temperature change near the surface. These negative values indicate the increase of opacity of the atmosphere and increase of the down-welling infrared radiation caused by the replacement compounds.

3.3 Atmospheric cooling rate

In order to study the vertical structure of the radiative effects caused by the compounds, the spectral cooling rate profiles were calculated. Figure 3 shows the results for the mid-latitude summer atmosphere containing no replacement compounds (background atmosphere). The spectral resolution of the calculation is 1.0 cm$^{-1}$. In this figure, blue and red colors represent cooling and heating, respectively. The names of the constituents which contribute to strong cooling and heating are indicated in the figure. The cooling and heating near the left and right axes are associated with CO$_2$ and H$_2$O, respectively. The heating in the stratosphere due to the $v_3$ band of ozone in 960–1080 cm$^{-1}$ and $v_1$ band in 1080–1180 cm$^{-1}$ are very impressive. The water vapor continuum primary contributes to the cooling below about 5 km, covering most of the atmospheric window region. The heating from 1250 to 1350 cm$^{-1}$ that occurs in the upper troposphere is due to CH$_4$ and N$_2$O.

The total cooling rate profile (hereafter, it is simply called cooling rate) can be obtained by integrating the spectral cooling rate profiles over the whole spectral range. In this study, it was carried out over a range from 700 to 1500 cm$^{-1}$, and results are shown in Fig. 4 for the 6 types of background atmosphere. The heating in the stratosphere and cooling in the troposphere are primary due to stratospheric ozone and

| Species | TPL | MLS | MLW | SAS | SAW | USS |
|---------|-----|-----|-----|-----|-----|-----|
| CFC-11: CC$_3$F | 3.53 | 3.47 | 2.65 | 3.29 | 1.75 | 3.84 |
| a1: (CF$_3$)$_3$COH | 4.61 | 4.49 | 3.30 | 4.15 | 2.22 | 4.72 |
| a3: -{(CF$_2$)$_4$CH(OH)} | 4.43 | 4.11 | 2.89 | 3.75 | 1.86 | 4.42 |

Units are $10^{-5}$ W/cm$^2$, and all values are negative.
TPL: Tropical, MLS: Midlatitude summer, MLW: Midlatitude winter, SAS: Subarctic summer, SAW: Subarctic winter, and USS: U.S. standard 1976.
December 1995 R. Imasu, A. Suga and T. Matsuno 1129

Water vapor (continuum), respectively. These cooling rate profiles were compared with those archived at the Carbon Dioxide Information and Analysis Center (CDIAC) database for intercomparison purposes. The results showed a good agreement.

The spectral cooling rates for the mid-latitude summer atmosphere containing replacement compounds are shown in Fig. 5, where data are shown as the difference from the background case shown in Fig. 3. In all cases, strong heating can be seen near the tropopause (15 km). The most interesting feature which should be pointed out is the strong cooling that occurs in the stratosphere for the compounds shown in (b) and (d). This cooling is caused by the overlapping of absorption bands between the compounds and stratospheric ozone. Note that this cooling can be seen even if the compound does not exist in the stratosphere, because the infrared radiation emitted from the surface or the lower troposphere is trapped by the compounds in the troposphere before reaching the stratospheric ozone layer.

This difference in feature of cooling more conspicuously can be seen in the cooling rate profiles shown in Figs. 6a and 6b for the 6 types of atmosphere. The fact which should be noticed is that the vertical profiles in the lower troposphere are very similar to each other for the two types of compounds in spite of

---

Fig. 3. Spectral cooling rate for the mid-latitude summer atmosphere which contain no replacement compounds (background atmosphere).

Fig. 4. Cooling rate profiles for the 6 types of model atmosphere which contain no replacement compounds (background atmosphere).
the difference in the stratosphere, and furthermore, the radiative forcings of these two compounds are almost the same, as shown in Table 1.

As an index which represents the degree of the cooling in the stratosphere, the ratio of the cooling rate at 30 km (in the middle of the stratosphere) to that at the tropopause height is calculated and listed in the last column of Table 1. In general, the cooling rate ratios for the compounds which cause the strong cooling in the stratosphere are relatively smaller (negative) than those of weak cooling cases. For example, the ratios for the compounds "a1" and "a3" are -0.41 and -1.12, respectively, and the difference correspond to that in the radiative feature shown in Fig. 6.

3.4 Spectral resolution dependency of radiative effects

The dependency of radiative forcing on the spectral resolution of the model calculations was studied. As an example, the change in the calculated radiative forcing is shown in Fig. 7 for a compound, where the relative values to those of CFC-11 are also plotted. These results show that the absolute value of radiative forcing gradually decreases as the resolution decreases, whereas the relative value to that of CFC-11 is almost the same up to about 50 cm\(^{-1}\). The vertical profiles of the cooling rate were also studied changing the spectral resolution. The results showed that the feature of the profiles began to change when the resolution exceeded about 50 cm\(^{-1}\) for some compounds. An example of the results is shown in Fig. 8. Therefore, we can say that a higher resolution than about 50 cm\(^{-1}\) would be recommended to calculate the radiative effects precisely.

3.5 Lifetimes in the atmosphere

The rate constants for the reaction with the OH radical calculated from HOMO energies are listed in the third column of Table 3, except for some compounds for which the estimation method for the reaction rate constant is not effective because of uncertainty of the empirically derived relationship be-
between the HOMO energy and reaction rate constant. The lifetimes calculated through Expression (7) are listed in the fourth column of Table 3. The lifetimes range from 0.10 to 11 years and all of them are shorter than that of CFC-11 for which photodissociation is the only degradation process.

3.6 HGWP s

Based on the radiative forcing and lifetime data, HGWP s for the compounds were evaluated through Expression (9), and the results are summarized in the last two columns of Table 3. The results show that most of the HGWP s are smaller than 0.1 (some of them are than 0.01) primarily due to their shorter lifetimes.
3.7 Comparisons with previously reported results

Intercomparisions of the radiative properties, lifetimes, and HGWPs for some HFCs, HCFCs, CFC-11, and MCF were made between our results and previously reported results by Fisher et al. (1990) and Colin et al. (1993) in order to examine the systematic error of the measurements of infrared absorption data and to examine the difference in the calculation of the radiative forcing by different types of atmospheric model. First, the integrated absorption cross sections are compared in Table 4. It shows that the absolute values of our study are somewhat larger than those from others. However, their relative values to that of CFC-11 are very similar to each other. The radiative forcing relative to CFC-11 is compared with those obtained from the radiative-convective model calculations by AER and Du Pont (Fisher et al., 1990) in Table 5. Our results agree well with those of AER and Du Pont in spite of the difference in type of calculation method. Comparisons of the lifetimes and HGWPs for the compounds are shown in Table 6 and Table 7, respectively. Note that the lifetimes of MCF are different in all references. However, as the lifetimes

Table 3. Rate constants for the reaction with the OH radical, lifetimes, and HGWPs of replacement compounds.

| Compound | Chemical formula | Reaction rate with OH at 296 K $\left(10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}\right)$ | Lifetime (year) | HGWP (Mol Basis) | HGWP (Weight Basis) |
|----------|------------------|------------------------------------------------|-----------------|------------------|---------------------|
| CFC-11   | CFCI$_3$         | 0.957                                          | 58             | 0.022            | 0.022               |
| MCF      | CH$_3$CCL$_3$    | 0.179*                                         | 31             | 0.49             | 0.53                |
| HFC-134  | CF$_3$CHF$_2$    | 0.406*                                         | 14             | 0.15             | 0.20                |
| HFC-141b | CH$_3$CCL$_2$F   | 0.545*                                         | 10             | 0.11             | 0.13                |
| HFCFC-225cb | CF$_2$CF$_2$CHCIF | 0.806*                                        | 6.9            | 0.14             | 0.093               |
| E-134    | CHF$_2$-O-CHF$_2$| 0.30 (2.53)                                    | 19 (2.19)      | 0.52 (0.062)     | 0.61 (0.073)        |

*Based on DeMore et al. (1994)
and HGWPs of the replacement compounds are inversely proportional to that of MCF according to expressions (7) and (9), we can easily obtain the rescaled values for each reference. The results show a certain measure of agreement after the re-scaling.

4. Discussion

The HGWPs obtained as the final results of our calculations for the replacement compounds are smaller than 0.1 owing to their shorter lifetimes, in spite of their larger absorption strengths. Therefore, we can say that these compounds can be the valid candidate as CFC replacements from a viewpoint of HGWP.

The lifetime of MCF is very important in this type of scaling method for estimating the lifetimes of chemical compounds. Although a value of 6.3 years had been generally used as the lifetime based on the ALE/GAGE analysis (Prinn et al., 1987), we adopted a different value of 5.8 years as the lifetime in this study. The lifetime was based on personal information from Dr. Ko who is a member of IPCC working group that the lifetime which will be adopted as a recommended value in the working group report will be revised based on the new ALE/GAGE data obtained through a new calibration method of data analysis.

Another important factor in estimating the lifetimes of compounds is the atmospheric mean temperature which determines the rate constant for the reaction between the compound and OH radical. In this study, the temperature was assumed to be 296 K as mentioned in Section 2.3, and this value was different from that recommended by Prather and Spivakovskiy (1990). The difference in HGWP caused by that in the temperature can be estimated from the temperature dependence factor \( \exp\left(\frac{E}{R}\right) \) of the Arrhenius form of reaction rate through the Expressions (7) and (9). The factor which is affected by the temperature in the Expression (9) is the ratio \( k_{\text{MCF}}/k_x \) of the reaction rate constants of MCF and a replacement compound \( x \). The value of \( E/R \) for MCF is 1750 (De More, 1994), and that for the replacement compound can be, for example, assumed to be a typical value of 1550. The ratios of the temperature dependence factors at 277 K and 296 K are respectively calculated as

\[
\exp\left(-\frac{1750}{277}\right)/\exp\left(-\frac{1550}{277}\right) = 1.97 \text{ (at 277 K)},
\]

\[
\exp\left(-\frac{1750}{296}\right)/\exp\left(-\frac{1550}{296}\right) = 2.06 \text{ (at 296 K)}.
\]

The difference between these ratios is about 5%. This error is not relatively large compared with those from other error sources.

The overlap problem of absorption bands has been discussed by some scientists (Ramanathan et al., 1985; Fisher, 1990). However, most of the discussions have been made only from a viewpoint of the surface temperature change or radiative forcing change. In this study, we pointed out that overlapping of absorption bands between the compound and ozone causes strong cooling in the stratosphere, even if the compounds exist only in the lower at-

Table 4. Integrated infrared absorption cross sections. The data in parentheses are values relative to that of CFC-11 in each reference.

| Species   | Present study | Gehring* | Magid* | Colin et al.** |
|-----------|---------------|----------|--------|----------------|
| CFC-11    | 2631          | —        | 2389   |                |
|           | (1.00)        | (1.00)   |        |                |
| HCFC-141b | 2226          | 1732     | 1912   | 2085           |
|           | (0.846)       | (0.800)  |        |                |
| HCFC-225cb| 4476          | —        | —      | 4191           |
|           | (1.701)       |          |        |                |
| HFC-134a  | 3619          | 3169     | 3272   | —              |
|           | (1.38)        | (1.37)   |        |                |
| HFC-125   | 4575          | 3908     | —      | 4334           |
|           | (1.74)        |          |        |                |
| MCF       | 1350          | 1184     | 1209   | —              |
|           | (0.513)       | (0.506)  |        |                |

Units are atm\(^{-1}\) cm\(^{-2}\) STP

*Fisher et al. (1990)
**Colin et al. (1993)

Table 5. Radiative forcing relative to that of CFC-11.

| Species    | Present study | AER* | Du Pont* |
|------------|---------------|------|----------|
| HCFC-141b  | 0.628         | 0.623** | 0.571   |
| HFC-134a   | 0.656         | 0.771** | 0.714   |
| HFC-125    | 0.888         | 1.08***| 0.895   |
| MCF        | 0.225         | 0.217** | 0.248   |

*Fisher et al. (1990).
**Gehring's Infrared data was used in Fisher et al. (1990).
***Magid's Infrared data was used in Fisher et al. (1990).
Comparing with the study by Clough and Iacono (1992), this disturbance in the vertical structure of the radiative effects is of the same order of magnitude as that which can be expected to be caused by a tens of percent increase of currently used CFCs assuming the proportionality of the effect to the concentrations of the chemicals. We would like to emphasize that it is important to examine the vertical structure of the radiative disturbance due to replacement compounds as much as to examine their GWPs (or HGWPs) in order to assess their environmental impacts comprehensively.

In earlier studies, most of the calculations of the radiative effects caused by CFCs and their replacements have been carried out at spectral resolutions of the order of 100 cm\(^{-1}\) to save calculation time (Briegleb, 1992; Colin et al., 1993). However, the results for the spectral-resolution dependency of the radiative effects shown in Section 3.4 indicate that the resolution has to be finer than about 50 cm\(^{-1}\) to calculate the radiative forcing and spectral cooling rate accurately. This point should be taken into consideration in future studies.

The only degradation process of the replacement compounds was assumed to be the reaction with the OH radical in this study. However, it may well be that these compounds can be degraded through the other processes such as rainwater dissolution (chemical degradation in rainwater or washout by rain) and ocean uptake because of their hydrophilicity. Furthermore, the compounds can be degraded by ultraviolet photolysis as much as CFCs in the atmosphere. The hydrolysis rate constants and photolysis rates are necessary in future studies to estimate the degree of the contribution of these degradation processes to the total removal of the compounds. As described in Section 2, the main error source in evaluating GWPs is uncertainty in estimating rate constants of the reaction between the compounds and the OH radical. However, it is technically difficult to reduce the estimation error at the present time.

Therefore, the experimental measurement of the reaction rate constants is a very important subject and the estimated data should be validated with the measured data. Furthermore, it is also important to measure the temperature dependency of the rate constants and infrared absorption cross sections in the next phase of research in which the vertical concentration profiles of the chemical compounds are calculated using photochemical reaction models in order to assess the more practical behavior of the compounds in the atmosphere.

In this study, the radiative disturbances caused by the degradation products produced through the reaction between the replacement compounds and the OH radical and subsequent reactions were not taken into consideration because the processes itself had not been well clarified. However, the radiative effects caused by the products should be considered as the parts of the effects originated in the replacement compounds. The studies on the radiative properties and chemical behavior of the degradation products are future problems.

### 5. Conclusions

Instantaneous radiative forcing was calculated for 5 fluoroalcohols, 30 fluoroethers, and 4 fluoroamines which have been proposed as the replacements for the currently used chlorofluorocarbons (CFCs) in refrigeration. The atmospheric lifetimes of the replacement compounds were also estimated under the assumption that the compounds are degraded only by the reaction with the OH radical. The rate constants used for the estimation were derived...
from Highest-occupied Molecular Orbital (HOMO) energies. Based on the radiative forcing and atmospheric lifetimes, halocarbon global warming potentials (HGWP) were evaluated for the compounds. Most of them were smaller than 0.1 owing to their shorter lifetimes in spite of their larger absorption strengths. These results indicate that these compounds could be valid candidates as replacements for currently used CFCs from a view point of HGWP.

The spectral cooling rate profiles were calculated for the replacement compounds to study the vertical structure of their radiative effects. It was found that overlapping of the absorption bands of a compound with those of ozone causes a significant cooling in the stratosphere, even if the compound does not exist in the stratosphere. This cooling does not directly relate to the HGWP values and the cooling rate profile in the troposphere. Therefore, it can be said that the vertical structure of the radiative effects caused by a replacement should be taken into consideration as well as HGWP or GWP values when we assess its environmental impacts correctly. In order to represent the degree of the cooling in the stratosphere one parameter defined as the ratio of the cooling rates at 30 km and the tropopause height was proposed.

Spectral-resolution dependency of the calculated radiative effects was also studied. The results show that the resolution should be finer than about 50 cm$^{-1}$ to calculate the radiative forcing and cooling rate precisely.

In the last part of this paper, we mentioned the other degradation processes of the replacement compounds and the radiative effects which might be caused by the degradation products produced through the reaction of the replacement compounds with OH radical and the subsequent reactions. These are very important problems for future studies.

Acknowledgments

This study was partially supported by New Energy and Industrial Technology Development Organization (NEDO) and Development of Global Environment Technology project of Agency of Industrial Science and Technology (AIT). The authors would like to express their hearty thanks to Dr. S.A. Clough, Dr. G. Anderson, Dr. L.S. Rothman, and their co-workers for their providing them with the FASCODE 3P program and HITRAN 92 database. The authors also wish to thank Dr. M. Ko and Dr. S.A. Clough of Atmospheric and Environmental Research, Inc. for their good advice on the calculations of the radiative properties and the lifetimes of the replacement compounds. The Carbon Dioxide Information and Analysis Center (CDIAC) database was used for comparison of the infrared radiation fluxes calculated for standard atmospheres.

References

Briegleb, B.P., 1992: Longwave band model for thermal radiation in climate studies. J. Geophys Res., 97, 11475-11485.

Colin., C.C.R., P.C. Simon and C. Granier, 1993: Infrared cross sections and global warming potentials of 10 alternative hydrohalocarbons. J. Geophys Res., 98, 10491-10497.

Clough, S.A., F.X. Kneizys, E.P. Shettle and G.P. Anderson, 1985: Atmospheric radiance and transmittance, paper presented at the Sixth Conference on Atmospheric Radiation, Am. Meteor. Soc., Boston, Mass., pp. 141-144.

Clough, S.A., R.D. Worsham, W.L. Smith, H.E. Revercomb, R.O Knuteson, G.P. Anderson, M.L. Hoke and F.X. Kneizys, 1989: in IRS'88: Current Problems in Atmospheric Radiation, J. Lenoble and J.F. Geleyn, Eds., A. Deepak, Hampton, Va., pp. 376-379.

Clough, S.A. and M.J. Iacono, 1992: Line-by-line calculation of atmospheric fluxes and cooling rates II: Application to carbon dioxide, ozone, methane, and the halocarbons. paper presented at the Eighth Conference on Atmospheric Radiation, Am. Meteor. Soc., Boston, Mass., pp. 547-549.

Clough, S.A., M.J. Iacono and J.-L. Moncet, 1992: Line-by-line calculation of atmospheric fluxes and cooling rates: application to water vapor. J. Geophys. Res., 97, 15761-15785.

Daniel J.S., 1995: On the evaluation of halocarbon radiative forcing and global warming potentials. J. Geophys. Res., 100, 1274-1285.

DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb and M.J. Molina, 1994: Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation Number 11, NASA Panel for Data Evaluation, Publ. 94-26, Jet Propulsion Laboratory, Pasadena, CA.

Fisher, D.A., C.H. Hales, W.-C. Wang, M.K.W. Ko and N.D. Sze, 1990: Model calculations of the relative effects of CFCs and their replacements on global warming. Nature, 344, 513-516.

Hansen, J., A. Lacis and M. Prather, 1989: Greenhouse effect of chlorofluorocarbons and other trace gases. J. Geophys. Res., 94, 16417-16421.

Intergovernmental Panel on Climate Change (IPCC), 1990: Climate change — The IPCC Scientific Assessment:— Report prepared for IPCC by working group 1. J.T. Houghton, G.J. Jenkins and J.J. Ephraums, Eds., Cambridge University Press, New York.

Intergovernmental Panel on Climate Change (IPCC), 1994: Radiative forcing of climate change: The 1994 report of the scientific assessment working group of IPCC. Cambridge University Press, New York, pp. 28.

Liou, K.N., 1980: An introduction to atmospheric radiation. International Geophysics Series, Vol. 26, Academic Press, London, pp. 93-97.

Molina, M.J., and F.S. Rowland, 1974: Stratospheric sink for chlorofluoromethanes: Chlorine atom-
catalysed destruction of ozone. Nature, 249, 810-814.
Prather, M. and C.M. Spivakovsky, 1990: Tropospheric OH and the lifetimes of hydrochlorofluorocarbons. J. Geophys. Res., 95, 18723-18729.
Prather, M.J., M. McElroy, S. Wofsy, G. Russell and D. Rind, 1987: Chemistry of the global troposphere: fluorocarbons as tracers of air motion. J. Geophys. Res., 92, 6579-6613.
Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser and R. Rosen, 1987: Atmospheric trends in methyl chloroform and the global average for the hydroxyl radical. Science, 238, 946-950.
Ramanathan, V., R.J. Cicerone, H.B. Singh and J.T. Kiehl, 1985: Trace gas trends and their potential role in climate change. J. Geophys. Res., 90, 5547-5566.

Shi Guangyu, 1992: Global warming potential due to chlorofluorocarbons and their substitutes. Chinese J. Atmos. Sci., 16, 240-248.
Stolarski, R.S. and R.J. Cicerone, 1974: Stratospheric chlorine: A possible sink for ozone. J. Chem., 52, 1610-1615.
Suga, A., Y. Mochizuki, Y. Gotoh, H. Ito, M. Takahashi, S. Yamashita, M. Aoyagi, A. Sekiya and S. Kondo, 1993: Estimated lifetimes of fluorinated ethyl methyl ethers in atmosphere. Chem. Exp., 8, 205-208.
Suga, A., Y. Mochizuki, N. Nagasaki, Y. Gotoh, H. Ito, S. Yamashita, T. Uchimaru, M. Sugie, A. Sekiya, S. Kondo and M. Aoyagi, 1994: Estimation of total infrared intensities of fluorinated ethyl methyl ethers. Chem. Letters, 1994, 2365-2368.

World Meteorological Organization, 1989: Scientific assessment of stratospheric ozone: 1989. Global ozone research and monitoring project-Rep. No. 20.

代替フロン物質の放射効果とハロカーボン温暖化係数

今須良一
(資源環境技術総合研究所)
須賀淳雄1
(地球環境産業技術研究機構)
松野太郎
(北海道大学大学院地球環境科学研究科)

現在使用されている冷媒用フロン類の代替物質として提案されている5種類のアルコール系物質、21種類のエーテル系物質、及び、5種類のアミン系物質について、瞬時放射強制力を計算した。また、これら21種類の物質の大気中での寿命を、最高被占率（HOMO）エネルギーから求めたOHラジカルとの反応係数に基づいて推定した。この放射強制力と大気中寿命をもとに、ハロカーボン温暖化係数（HGWP）を求めた。ほとんどの物質のHGWP値は、大気中寿命が短いことが起こって、0.1よりも小さい値であった。この結果は、HGWP値で見る限り、これらの物質が現在使用されているフロン類の代替可能物質となり得ることを示している。

これらの代替物質の放射効果の鉛直構造を調べるため、波長別大気冷却率の鉛直分布を計算した。その結果、代替物質の赤外吸収バンドがオゾンの吸収バンドと重なる場合には、例えばその物質が成層圈に存在しない場合でも、成層圈が非常に冷却されることがわかった。この冷却はHGWPの値や対流層での大気冷却率分布には直接は関係していない。したがって、ある代替物質に対する環境影響評価を行ううとする場合、GWPやHGWPを含めると、その物質による放射効果の鉛直構造も考慮される必要があると言うことができる。本研究では、この成層圈での冷却の程度を示す一つの指標として、高度30kmと層界面に於ける冷却率の比の値を用いることを提案した。

また、計算により求められる各種放射効果の波数分解能依存性を調べた。その結果、放射強制力や冷却率を正確に計算するためには、波数分解能は50cm^{-1}程度よりも良くなければならないということがわかった。

1現在所属：旭硝子株式会社、大阪 530