

Photoabsorption Cross Sections of CFC-Related Molecules in the Ultraviolet Radiation Region

Isao H. SUZUKI and Masaki KOIKE

In order to estimate life times through photodissociation for chloro-fluoro-carbon molecules and a freon-alternative compound at several altitudes, photoabsorption cross sections of these molecules have been measured in the ultraviolet radiation region. Monochromatized synchrotron radiation and a temperature-variable long absorption cell were used for the measurements, which were carried out in two modes, wavelength scanning and gas-density changing. The cross sections for CFC-112 and CFC-114 at a low temperature show lower values than those at room temperature above about 195 nm. The absorption spectrum of HFC-134a indicates that this molecule has cross sections lower than 10^{-22} cm² in the ultraviolet region. The photodissociation life times were estimated at the equinox above the Equator using calculated day-averaged intensities of solar ultraviolet radiations.

§1 Introduction

Expansion of human activities and of energy demand largely consumes fossil fuels, which is supposed to increase the concentration of CO₂ in the atmosphere. Many people are afraid that this increase is provoking temperature rise and climate change in tens of years later. The main origin of the temperature rise is the absorption of terrestrial radiations by atmospheric molecules in the infrared region (green-house effect). Then all molecules absorbing infrared radiations bring about some effect on the temperature rise. Molecules having absorption band in radiation regions different from that of CO₂ are presumed to make a large effect although those having the same absorption band with CO₂ indicate a small effect. The temperature rise was predicted to be yielded by an increase in concentrations of several trace gases, for example, CH₄ and chloro-fluoro-carbon molecules (CFC).¹⁾ The summed temperature rise by all the trace gases was presumed to be slightly larger than that by CO₂ only. The effect per one molecule for these gases is several orders greater than that of CO₂. These gases are inert in chemical reactivity, and a variety of

observations showed that the height distributions of their concentrations are constant in the troposphere.²⁾ These findings indicate that their life times are very long in the troposphere. Many of those gases are expected to dissociate through absorption of solar ultraviolet radiation or to react with radicals in the stratosphere.^{3,4)} Hence the photodissociation rate is a very important factor in estimation of their lives, which play a critical role in determining a potential of the green-house effect.

The present study has been initiated in order to estimate photodissociation rates of green-house effect gases and related molecules in upper atmospheres. The estimation needs accurate data on photoabsorption cross sections of the molecules at a low temperature. These cross sections have been measured using a long absorption cell connected with monochromatized synchrotron radiation for CFC-112, CFC-114 and HFC-134a in the region of 180 nm through 230 nm.

§2 Experimental

Arrangement for measurements of photoabsorption cross sections was described previously, and is here

indicated briefly.⁵⁻⁷⁾ Synchrotron radiation was monochromatized using a Seya-Namioka type monochromator with vertical dispersion, providing an ultraviolet radiation having nearly parallel characteristics. The wavelength scanning interval of the ultraviolet radiation was about 0.1nm at measurements described below. A photoabsorption cell of 483mm long and of 19mm ϕ was mainly utilized. The cell was positioned at 1.5m behind the post focusing mirror. The cell was equipped with two windows of CaF₂ for entrance and exit of the monochromatic radiation beam, with a capacitance manometer, and with some ports for gas introduction, sampling and evacuation. A cold bath surrounds the cell, the temperature of which was monitored with a thermister fixed to the outer wall of the cell. The bath was supplied with ethyl alcohol, which was made circulation with a magnetic stirrer. The cold bath was cooled down and maintained at a low temperature by a cooling device (Eyela Cool EC-80) and an additive resistive heater pipe. The bath temperature was controlled by a computer with an uncertainty of ± 0.5 K. About half of the incident ultraviolet radiation was detected with a Si-photodiode, and the transmitted radiation was observed with another Si-photodiode.

Sample gases with research grade purity were purified through a cycle of evaporation and solidification in vacuum using some cold reagent or liquid nitrogen traps. This cycle was repeated several times on the basis of examination of impurities using a quadrupole mass spectrometer. The purified gases were supplied into the cell through a needle valve, but the gases were diluted with He before its supply when the low density gases were required owing to strong photoabsorption ability. The measurements of photoabsorption spectra were usually carried out at 0.1nm interval from 180nm to 230nm in wavelength. Before and after the spectrum measurement, the transmission spectra were observed for the cell evacuated sufficiently. This observation was made for calibration of detectors. When the signal intensities of the incident radiation and of the transmitted radiation are expressed with I_0 and I_1 , respectively, the following equations give the calibrated signals.

$$I_0 = I_0(n=n) / I_0(n=0) \quad \dots (1)$$

$$I_1 = I_1(n=n) / I_1(n=0) \quad \dots (2)$$

In the above equations, n denotes the number density of the sample molecule and 0 means zero density(empty). The photoabsorption cross section at a temperature T and a wavelength λ was represented with the following.

$$\sigma(\lambda, T) = n^{-1} \cdot L^{-1} \cdot \ln\{I_0(\lambda, T) / I_1(\lambda, T)\}, \quad \dots (3)$$

where L denotes the length of the optical path.

Another type of measurements were performed for obtaining the photoabsorption cross section. The molecular density was varied for a fixed wavelength and then the intensity of the transmitted light I_1 was measured. The logarithm of the intensity I_1 was plotted against the molecular density. The slope of this plotting equates the reciprocal of the product of the cross section and the path length. Most of these plottings showed that datum points go along with a straight line in the region of the optical density of 0.1 through 0.8. The obtained values for the cross section are usually in agreement with each other in the both experimental modes, molecular density changing and wavelength scanning.

§3 Results and Discussion

3.1 Photoabsorption Cross Section

3.1.1 CFC-112 (CCl₂FCCL₂F)

The molecule CFC-112 is formed through substitution of one Cl atom with one F atom from CFC-113. Then chemical reactivity and optical characteristics are supposed to be similar to those of CFC-113. This fact means that depletion of CFC-112 in the atmosphere is governed by photodissociation processes induced by solar ultraviolet radiations. Photoabsorption cross sections of many CFC-compounds were obtained by Hubrich and Stuhl, who used a deuterium lamp as a light source.³⁾ However they did not report that of CFC-112. The photoabsorption cross section of this molecule has been measured at room temperature by the present authors.⁶⁾ The character of that cross section was close to that expected through the halogen atom substitution from CFC-113.

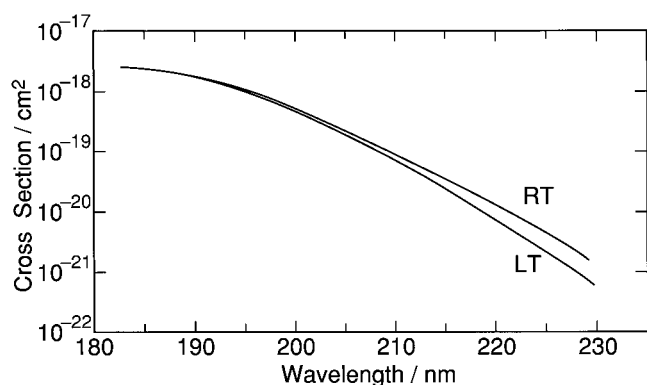


Fig.1 Photoabsorption cross sections of CFC-112 in the ultraviolet radiation region.
RT: Room temperature. LT: 241K.

Figure 1 shows the cross sections of CFC-112 at room temperature (RT) and at 241K (LT) in the region of 185 nm to 225 nm. At shorter wavelengths the obtained cross sections are an order of 10^{-18} cm^2 and those at RT and LT show both the same values. The electronic transition connected to this photoabsorption is supposed to be Cl3p lone pair orbitals because these are the shallowest orbitals.⁸⁾ This molecule includes 4 Cl atoms, i.e., 8 Cl3p lone pair orbitals, and these orbitals interact with one another. Some orbitals are deeply stabilized and others become shallower through interaction among the same type orbitals. This interaction yields at least one considerably shallow orbitals, which is responsible for an optically allowed transition in the ultraviolet radiation region. The cross sections exhibit a decrease monotonically as the wavelength becomes long, and those show lower values in the long wavelength region than 10^{-20} cm^2 .

Table 1 lists values for the photoabsorption cross

Table 1 Photoabsorption cross sections of CFC-112 in the ultraviolet radiation region (in units of cm^2).

Wavelength			
/nm	299K	241K	Ratio*
185	2.3×10^{-18}	2.3×10^{-18}	1.00
190	1.68×10^{-18}	1.64×10^{-18}	0.98
195	9.2×10^{-19}	8.9×10^{-19}	0.97
200	4.6×10^{-19}	4.1×10^{-19}	0.89
205	2.0×10^{-19}	1.64×10^{-19}	0.82
210	8.7×10^{-20}	5.6×10^{-20}	0.64
215	3.7×10^{-20}	2.2×10^{-20}	0.59
220	1.37×10^{-20}	5.9×10^{-21}	0.43
225	4.5×10^{-21}	2.0×10^{-21}	0.44
230	1.3×10^{-22}	5.8×10^{-22}	0.44

* : Ratio of the cross section at 241K to that at 299K.

sections at RT and LT as well as the ratios between those values. The ratio becomes lower with an increase in the wavelength, and exhibits a lower value than 0.5 above 220 nm. At room temperature, there is no molecule in electronically excited states, but some molecules are excited at vibrational and rotational modes. These excited states have a potential to change an electronic transition probability, and these states can induce more strongly the transition at long wavelengths than the ground state. Another possibility originates from a change in the geometrical conformation in an electronically excited state, into which the molecule turns through the transition. This conformation change is presumed to give rise to an increase in the photoabsorption probability for vibrationally and rotationally excited states.⁹⁾ The population of the excited states is larger at RT than LT, and the difference in the population between RT and LT is larger for highly excited states than low excited states. These effects can explain the present finding on the difference in the cross sections. At longer wavelengths, which correspond to a tail of the electronic transition, the population difference in excited states reflects more clearly the difference in the cross sections than shorter wavelengths.

3.1.2 CFC-114 ($\text{CClF}_2\text{CClF}_2$)

The compound of CFC-114 has been used as a foaming reagent and a cooling reagent. This compound has a capability for depleting the ozone layer in the stratosphere, and then has been regulated by an international protocol on the protection of the ozone layer. Besides the problem of the ozone layer, this molecule is supposed to make the green-house effect. The potential of green-house warming was estimated for several molecules by UNEP/Ozone-layer Protocol, WG II. This potential of CFC-114 is about 4 with respect to 1.0 for CFC-11. Photoabsorption cross section of CFC-114 at RT was examined previously in the ultraviolet radiation region by two groups.^{3,6)} The data in our study showed slightly lower values at short wavelengths and considerably lower at longer wavelengths than those by Hubrich and Stuhl. Since it is important to obtain reliable data, the present authors have measured the photoabsorption cross sections at RT and a low temperature. The results are

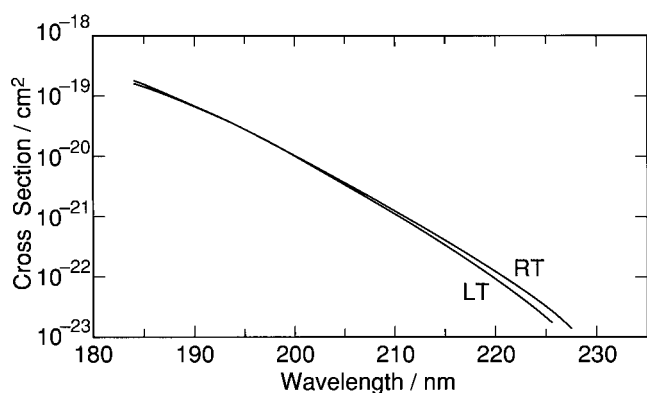


Fig.2 Photoabsorption cross sections of CFC-114 in the ultraviolet radiation region.

RT: Room temperature. LT: 234K.

Table 2 Photoabsorption cross sections of CFC-114 in the ultraviolet radiation region (in units of cm^2).

Wavelength			
/nm	292K	234K	Ratio*
185	1.34×10^{-19}	1.38×10^{-19}	1.03
190	6.2×10^{-20}	6.1×10^{-20}	0.98
195	2.6×10^{-20}	2.4×10^{-20}	0.92
200	9.8×10^{-21}	9.0×10^{-21}	0.92
205	3.3×10^{-21}	2.9×10^{-21}	0.88
210	1.26×10^{-21}	9.4×10^{-22}	0.75
215	4.1×10^{-22}	3.0×10^{-22}	0.73
220	1.29×10^{-22}	9.2×10^{-23}	0.71
225	3.4×10^{-23}	1.9×10^{-23}	0.56

* : Ratio of the cross section at 234K to that at 292K.

exhibited in **Fig.2** for the wavelengths between 185 nm and 225 nm. **Table 2** lists the values of cross sections at several wavelengths, together with the ratio between the cross sections at LT and RT.

Both cross sections show a monotonous decrease as the wavelength becomes long. The rate of this decrease, which exhibits a change of about 4 orders in magnitude between 185 nm and 225 nm, is steeper than that of CFC-112. In the instance of CFC-112, the cross section decreases by about 3 orders in the same wavelength interval. The highest occupied molecular orbital of CFC-114 is supposed to be a $\text{Cl}3p$ lone pair orbital, which is responsible for optically allowed transition in a long wavelength region.⁸⁾ Since the number of Cl atoms within the molecule is smaller at CFC-114 than CFC-112, the shallowing effect of the orbital is presumed to be weaker at CFC-114 than CFC-112. Therefore, in CFC-114 the allowed transition probably takes place at slightly shorter wavelengths than the present measurement region, i.e. vacuum

ultraviolet radiation region. It is presumed that the photoabsorption has been observed at present as a tail of the optically allowed transition. Thus the value of the cross section is about one order lower at the shortest wavelength and the decrease rate into longer wavelengths is considerably larger in comparison with those of CFC-112. The cross section at LT exhibits a slightly higher value at 185 nm but becomes lower above 190 nm than that at RT. The ratio of the cross sections between LT and RT exhibits a decrease with increasing wavelength. This finding comes from the population difference in vibrationally and rotationally excited states between RT and LT. However, the ratio shows a higher value at the longest wavelength than 0.5, which is higher than that of CFC-112. This finding is presumably connected with the difference between vibrational frequencies related to C-F bond and C-Cl bond.¹⁰⁾ At the room temperature the population of the vibrationally excited states in the C-F bond is lower than the C-Cl bond, which yields higher ratio value at CFC-114 than CFC-112.

3.1.3 HFC-134a($\text{CF}_3\text{CH}_2\text{F}$)

This molecule (1, 1, 1, 2-tetrafluoroethane) is one of the most promising alternatives for CFC-compounds, in particular a candidate of substitution for CFC-12. The ozone depletion potential of HFC-134a was estimated to be zero because this molecule includes no Cl atom. Recent study confirmed that HFC-134a is safe for the ozone layer.¹¹⁾ The greenhouse warming potential of this molecule was reported to be about 0.25. This value comes from a short life time in the atmosphere because this molecule can react with OH radical and turn into another compound. The rate constant of this reaction was estimated to be about $8 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$ at RT, which is similar to those of HCFC-123 and CH_3Cl with OH radical.^{12,13)} However, it is desirable to examine the possibility that a part of the HFC-134a emitted into the atmosphere reaches the tropopause and decomposes through photoabsorption of solar ultraviolet radiations.

Photoabsorption cross sections of HFC-134a at RT and LT are shown for the wavelength region of 155 nm and 190 nm in **Fig.3**. The cross sections are very small in comparison with CFC-compounds. Even at 160 nm, vacuum ultraviolet radiation region, the cross

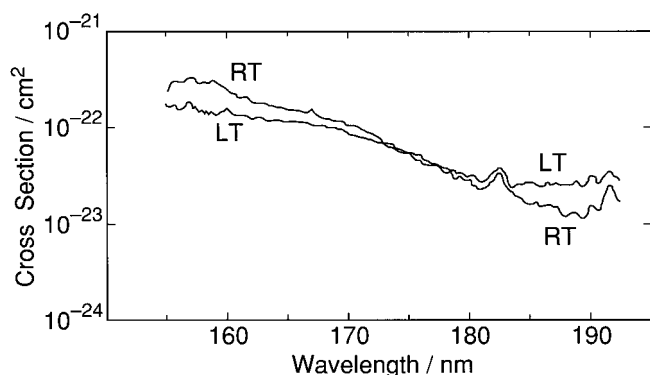


Fig.3 Photoabsorption cross sections of HFC-134a in the wavelength region of 155 nm through 190 nm. RT: Room temperature. LT: 237K.

sections are an order of 10^{-22} cm^2 , and these values decrease moderately to an order of 10^{-23} cm^2 at longer wavelengths. The characteristics of the cross section at LT seem to be similar to those at RT, but the cross section at LT is slightly lower at shorter wavelengths and higher at longer wavelengths than that at RT. These low cross section values indicate that an optically allowed transition does not happen in this wavelength region. This molecule does not contain Cl atoms but consists of C, F and H atoms. The highest occupied molecular orbital is supposed to be the C-C bonding orbital or C-H bonding orbitals.⁸⁾ Contrary to the Cl3p lone pair orbital, these orbitals are deeply stabilized and thus are related to photoabsorption in the vacuum ultraviolet region. As expected from those of C_2H_6 , C_2F_6 and related molecules, the allowed electronic transition is presumed to happen at wavelengths shorter than 150 nm.¹⁴⁻¹⁷⁾ The photoabsorption in the present region is probably a kind of the tail of an absorption band. The cross section data are listed in **Table 3**. However a part of decrease in the transmitted ultraviolet radiations in the measurement possibly comes from scattering but is not yielded through photoabsorption. Thomson type scattering can be approximated with the classical electron orbit and the number of electrons. This molecule has 38 valence electrons, and this cross section is about 2×10^{-23} cm^2 . Since this theory assumes interaction between a photon and a free electron, the estimated value is merely an approximate measure. Then the photoabsorption cross section shown in Table 3 and Fig.3 probably includes a slight contribution from the scattering.

The spectrum observed at RT in a longer wavelength region is shown in **Fig.4**. That at LT is

Table 3 Photoabsorption cross sections of HFC-134a in the ultraviolet radiation region (in units of cm^2).

Wavelength	299K	237K	Ratio*
/nm			
155	2.4×10^{-22}	1.9×10^{-22}	0.79
160	2.4×10^{-22}	1.7×10^{-22}	0.71
165	1.5×10^{-22}	1.1×10^{-22}	0.73
170	1.0×10^{-22}	9.0×10^{-23}	0.90
175	5.4×10^{-23}	5.4×10^{-23}	1.0
180	2.8×10^{-23}	2.8×10^{-23}	1.0
185	1.6×10^{-23}	2.0×10^{-23}	1.2
190	1.6×10^{-23}	2.0×10^{-23}	1.2

* : Ratio of the cross section at 237K to that at 299K.

very close to the present spectrum. It seems that peaks and valleys appear periodically in the spectrum. The wavelengths corresponding to the peaks are listed in **Table 4**, together with intervals of peaks which are expressed with the wavenumber in units of cm^{-1} . The wavenumber was calculated as follows.

$$w(1) = \{1/\lambda(p_1) - 1/\lambda(p_2)\}, \quad \dots(4)$$

where p_1 and p_2 denote the successive peaks in the spectrum. The intervals range 373 cm^{-1} through 431 cm^{-1} , and the average wavenumber is 399 cm^{-1} . The intervals at longer wavelengths are larger in average than those at shorter wavelengths, and the trend in the interval variation suggests an occurrence of excitation of some vibrational mode. The average interval is close to the wavenumber of CCF-deformation vibration of $\text{CH}_3\text{CH}_2\text{F}$.¹⁰⁾ There seems no available data on the vibrational frequency of HFC-134a.¹⁸⁾ One reasonable explanation is that the spectral peaks are connected with vibrational excitation of the CCF-deformation

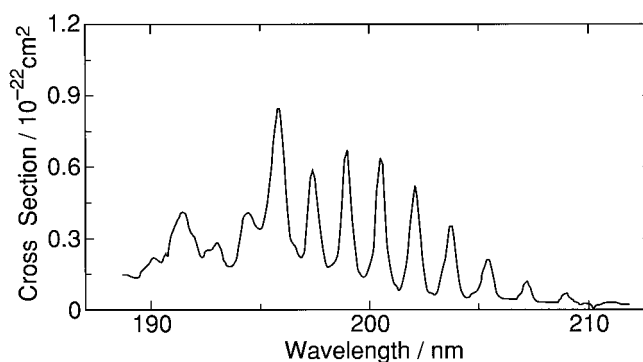


Fig.4 Photoabsorption spectrum of a molecule in the wavelength region of 190 nm through 211 nm. Note the discussion in text.

Table 4 Peak wavelengths in the photoabsorption spectrum of a molecule*.

Peak wavelengths /nm	Intervals of peaks /cm ⁻¹
190.1	385
191.5	406
193.0	373
194.4	394
195.9	388
197.4	407
199.0	376
200.5	395
202.1	413
203.8	382
205.4	423
207.2	416
209.0	431
210.9	

* : Note the discussion in text.

mode of HFC-134a, which takes place simultaneously with an electronic transition of optically forbidden character.

However, another possibility cannot be ruled out that the peaks originate from an impurity mixed in the sample. The purchased sample gas was a purity of 99 % in nominal. The sample gas was used after several cycles of evaporation and solidification. Examination through a mass spectrometer indicated that an impurity was about 0.1 % or less. A candidate of the impurity is a CFC compound and related molecules, which have a similar chemical feature. It is necessary that photoabsorption of this compound happens more strongly in this wavelength region than the sample by 3 orders or more. It is also required that the impurity molecule has oscillatory absorption structures in this wavelength region. Most of HFC-molecules are supposed to exhibit no large photoabsorption cross sections in this wavelength region. Many HCFC-molecules and CFC-molecules have no oscillatory structures in the region of interest. Therefore there is little possibility that some CFC-related molecules included as an impurity in the sample gas during measurements have yielded the spectrum with the oscillatory structure. The measurements under different gas densities indicated that the obtained values for the cross sections are independent of the

density of HFC-134a. This fact means that the contamination of the absorption cell itself makes little effect on the spectrum measured. Occasionally second order radiations make a spurious effect in the experiment using SR. However this possibility is ruled out because the present measurement utilizes CaF₂ windows for the cell, which absorb completely vacuum ultraviolet radiations around 100 nm. In conclusion, many reasons support that the spectrum in Fig.4 shows that of photoabsorption of HFC-134a, although one cannot deny completely that it is a spectrum of some impurity.

3.2 Life Times through Photodissociation

It is necessary to obtain absolute intensities of solar ultraviolet radiations at several altitudes for estimation of photodissociation life times of CFC compounds. Since the observed data of those intensities are limited, the intensities of spectral distributions have been calculated using the results observed with a launched rocket at a height of about 60 km.¹⁹⁾ In this calculation, the decrease in the solar radiation is brought about through the photoabsorption by O₂ and O₃ existing in the stratosphere. The photoabsorption cross sections and the concentrations of these molecules at several altitudes were cited from the literature.²⁰⁻²³⁾ Day averaged radiation intensities were derived from the intensities at the vertical incidence to the earth, in which effective path lengths of the solar radiations in the atmosphere, depending on the height of the solar position, were considered at 15° intervals. The radiation spectral distributions calculated at the equinox above the Equator show a minimum around 250 nm at an altitude of 30 km, which originates from the Hartley continuum absorption of O₃. Near the tropopause the spectral distributions have a maximum around 210 nm and considerable intensities above 280 nm. On account of the photoabsorption cross section of CFC compounds, the solar radiations around 200 nm play an important role in photodissociation processes of these molecules.

The photodissociation life times were calculated at some altitudes using the measured photoabsorption cross sections and the computed day-averaged solar radiation distributions. The quantum yields for dissociation were assumed to be 1.0 in all the

Table 5 Photodissociation lives of CFC-related molecules at several altitudes (in units of year).

Altitude /km	CFC-112	CFC-114	HFC-134a	CFC-12	CFC-113	HCFC-123	N ₂ O
10	2×10 ³	8×10 ⁴	4×10 ⁷	1×10 ⁴	1×10 ⁴	1×10 ⁴	8×10 ⁴
20	2	80	4×10 ⁴	14	13	10	60
30	0.1	3	2×10 ³	0.5	0.5	0.4	2

wavelengths for all the molecules. **Table 5** lists the life times through photodissociation for CFC-112, CFC-114, HFC-134a, as well as those for CFC-12, CFC-113, HCFC-123 and N₂O. The lives of the latter group of molecules were estimated previously,⁶⁾ but some mistake was recently found in truncation procedure for the integration of photodissociation rates about the wavelength. Those lives have been calculated again, which are included in Table 5. At 10 km all CFC-molecules show considerably longer lives than 10³ years. This finding indicates that these molecules can reach the tropopause without any loss owing to low reactivity with the OH radical. The lives of CFC-112 and CFC-114 are shorter and longer than CFC-113 at all altitudes, respectively. This result comes from the order of the magnitude of photoabsorption cross sections, which originates from the substitution of Cl atom to F atom in these molecules. At 20 km lives of CFC-112 and CFC-114 are 2 and 80 years, and those are 0.1 and 3 years at 30 km, respectively. The lives of HFC-134a listed in Table 4 are the shortest limit for photodissociation because the cross section listed has a possibility that a part of contribution comes from scattering. The HFC-134a has the longest photodissociation life among the molecules studied. This result comes from the low cross section of this molecule in the ultraviolet radiation region. Even at 30 km the life time is longer than 10³ years. This finding indicates that the atmospheric life of HFC-134a is governed by the reaction with OH radical. The present results correspond to the life times of the molecules at the equinox above the Equator. The temperature varies with the season and the latitude, which induces a change in the photoabsorption cross section. However the cross sections themselves do not change appreciably with temperature in the wavelength region which is mainly responsible for photodissociation. The effective path length varies with the season and the

latitude because the height of the sun changes. The mesh intervals in the present calculation are relatively large, and then the present estimation is presumed to be approximate. In addition, aerosols have a possibility to slightly decrease the solar radiations near the tropopause through scattering.²⁴⁾ This possibility is not considered in the study here because quantitative estimation of this effect is difficult at present.

§4 Summary

Photoabsorption cross sections of CFC-molecules and HFC-134a have been determined in the ultraviolet radiation region using monochromatized synchrotron radiation. HFC-134a was found to show a very small cross section in the present wavelength range, which is supposed to originate from no inclusion of Cl atoms in this molecule. The photodissociation life times were estimated for these molecules using the measured photoabsorption cross sections and the calculated solar radiation intensities at several altitudes. The lives for these molecules are longer than 10³ years at 10 km.

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The Authors



Isao H. SUZUKI

Quantum Radiation Division

E-mail: isuzuki@etl.go.jp

Researches on standardization of soft X-rays, dynamical behavior of inner-shell excited molecules, estimation of life times of green-house gases in the atmosphere, and fabrication of X-ray focusing devices, and administrative work on traceability of the national standards of ionizing radiations.



Koike MASAKI

Quantum Radiation Division

E-mail: koike@etl.go.jp

Researches on fabrication and characterization of novel X-ray devices and optics related to synchrotron radiation, and on multidimensional measurements of X-rays.