

### B-4.3 Studies on Photodissociation Rates of Atmospheric Compounds

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**Abstract** In order to estimate photodissociation rates of greenhouse gases at several altitudes, photoabsorption cross sections of these compounds have been measured in the ultraviolet region. Day-averaged intensities of solar ultraviolet radiation at several altitudes were calculated using the literature data for equinox in a latitude of 0°. Photodissociation rates were estimated using the observed cross section data and the calculated radiation intensities. Quantitative studies on the quantum yields of the photodissociation process have been performed using the two-color laser induced fluorescence method, the electron-impact ionization mass spectrometer and the excimer laser photolysis of shock heated samples. The quantum yields for the photolysis (193nm) of C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>O, CCl<sub>4</sub> and so forth were decided.

**Key Words** Greenhouse gases, Photoabsorption cross-section, Solar ultraviolet radiation, Quantum yield, Laser-induced-fluorescence

#### I. Introduction

The concentration of CO<sub>2</sub> in the atmosphere is presumed to increase owing to expansion of human activities and of energy demand, which largely consume fossil fuels. Many scientists are afraid that this increase is provoking temperature rise and climate change in tens of years later. The temperature rise is also brought about by an increase in concentrations of several trace gases, for example, CH<sub>4</sub> and chloro-fluorocarbons. These compounds are inert and the height distributions of their concentrations are constant in the troposphere, indicating that their life times are very long. Many of those gases are expected to dissociate through absorption of solar ultraviolet radiation or to react with radicals in the stratosphere. The photodissociation rate is a very important factor in estimation of their lives, which play a critical role in

determining a potential of green-house-effects.

## 2. Research Objective

The present study was initiated in order to estimate precisely photodissociation rates of green-house-effect gases and related compounds in the stratosphere. The estimation requires accurate data on photoabsorption cross sections of the compounds at stratospheric temperature, ultraviolet solar radiation at several altitudes, and quantum yields of photodissociation of the compounds. These data are being measured and/or calculated using a long absorption cell connected with synchrotron radiation, a laser excited fluorescence detection instrument and so forth.

## 3. Research Methods

Synchrotron radiation is monochromatized using a monochromator of Seya-Namioka type, providing an ultraviolet radiation source. Focusing characteristics of output photons were changed to a near-parallel beam so as to match a long photoabsorption cell. The design about this change was based on a ray-tracing calculation, and a re-focusing mirror was fabricated, whose shape is toroidal ( $R_v=4.06\text{m}$ ,  $R_h=0.822\text{m}$ ).

The long cell has been designed and constructed, which are 2 m long and 19 mm in diameter. The cell is surrounded with cold bath, of which temperature can be decreased to  $-60^\circ\text{C}$  and be maintained at a pre-set value by a personal computer. Preliminary measurements on photoabsorption spectra and cross sections of  $\text{N}_2\text{O}$  and chloro-fluoro-carbons were done with 1Å intervals in the ultraviolet radiation region. The obtained results are nearly in agreement with the data reported at 50Å intervals in the literature,<sup>1)</sup> in the wavelength region where the cross sections are not extremely small.

For pursuit of photodissociation reaction of the atmospheric compounds, instruments of simultaneous excitation with excimer-laser and chemical shock-waves and of combined detection with laser-induced fluorescence-apparatus and mass spectrometer were modified and tuned. Absolute concentrations of radical species produced in the UV photolysis were measured by combining E-I mass spectrometry, VUV resonance absorption, VUV laser induced fluorescence, and visible-to-UV laser induced fluorescence, together with a proper chemical titration method.<sup>2)</sup> In these experiments, the absorption profiles and intensities of Lyman- $\alpha$  lines for H and D atoms were taken as the standards of deciding their absolute concentrations. By measuring Lyman- $\alpha$  line absorption and LIF intensity of H and D atoms simultaneously, the correlation for the LIF intensity against absolute concentration of H or D atoms was decided. The relation between LIF intensity and absolute concentration of existing radical species was then decided by conducting simultaneous measurement of LIF intensities for H (or D) and for radicals in the chemical reaction systems such as,  $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$  or  $\text{CH}_3\text{OD} + 193 \text{ nm} \rightarrow$

CH<sub>3</sub>OD + H. Absolute concentrations of radical species which could not be detected by LIF were also decided with the similar technique by using E-I mass spectrometer.

#### 4. Results and Discussion

The photoabsorption cross sections were measured for chloro-fluoro-carbon molecules (CFC-12, -13, -113) and N<sub>2</sub>O in the ultraviolet radiation region at the room and the stratospheric temperatures. That of CFC-13 is  $5 \times 10^{-21} \text{cm}^2$  at 1,800Å and  $8 \times 10^{-22} \text{cm}^2$  at 2,050Å for the room temperature, but that for the stratospheric temperature was found to be lower than half of the that for the room temperature at 2,050Å. The cross section of N<sub>2</sub>O is  $1.2 \times 10^{-19} \text{cm}^2$  at 1,800Å and  $1.1 \times 10^{-22} \text{cm}^2$  at 2,300Å for the room temperature. The decrease in the cross section at the low temperature is similar to those of CFC's. These results are the same as the literature data in most instances, but some data points in the latter were found to be unreliable.

Concentrations of O(<sup>3</sup>P) produced in the photodissociation of O<sub>2</sub> and of CO<sub>2</sub> by 193 and 248 nm laser were measured by using atomic resonance absorption spectroscopy behind reflected shock waves over 1600-2500 and 1500-2700 K temperature ranges, respectively. The observed yield of O atoms and its time dependence in the photolysis of O<sub>2</sub> were found to agree very well with the calculation based on RKR potentials for the transition, B<sup>3</sup>Σ<sub>u</sub><sup>-</sup> ← X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>. It was concluded that the observed temperature dependence (E<sub>a</sub>=30.9 kcal/mol for the photolysis of O<sub>2</sub> by 248 nm excitation, and E<sub>a</sub>=13.6 kcal/mol for CO<sub>2</sub> excited at 193 nm, respectively) represented the vibrational energy of O<sub>2</sub> and CO<sub>2</sub> in the ground electronic states, from which absorption of UV light took place, and strong selectivity of the vibrational energies for the process was indicated (v<sup>\*</sup>=2 and v<sup>\*</sup>=7 for 193 and 248nm absorption, respectively). For the photodissociation of CO<sub>2</sub>, vibrational excitation of asymmetric stretching mode of v<sup>\*</sup> = 2 were supposed to strongly enhance the absorption of the electronic ground state to <sup>1</sup>B<sub>2</sub> level by 193 nm; the 193 nm excitation of CO<sub>2</sub> was successively photodissociated to form CO + O(<sup>3</sup>P) directly via the Landau-Zener transition to the <sup>3</sup>B<sub>2</sub> repulsive potential.

With the calibration technique newly developed here, the quantum yields of the 193 nm photolysis of N<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>OH, HNCO, and CCl<sub>4</sub> were measured. Table 1 shows the results obtained here for quantum yields of photolysis. The rate constants of the reaction of fluoromethane (CH<sub>3</sub>F and CHF<sub>3</sub>) with oxygen atom were also measured via the high temperature laser photolysis method for the first time. The rate constants were found to be consistent with the Evans-Polanyi rule in the series of reactions of alkanes with oxygen atom.

Intensities of ultraviolet radiation at several altitudes were calculated in consideration of decrease by photoabsorption of O<sub>2</sub> and O<sub>3</sub> using the observed data of solar radiation at the upper atmosphere, photoabsorption cross sections of these gases, and mixing ratios of atmospheric components. Day-averaged intensities were derived on

account of effective path length depending on the height of the solar position. Life time of N<sub>2</sub>O for photodissociation was estimated to be shorter than 1 month at 40 km and about 50 years at 20km. That of CFC-113 was about 1 month at 40km and about 20 years at 20km. Those for all the molecules studied here were longer than 10,000 years at the troposphere.

(References)

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Table 1. Observed quantum yields of molecules at 193nm photolysis.

SPECIES	PROCESS	$\Phi$ at 193nm	METHOD	$\sigma/cm^2$ at 193nm
C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> + h $\nu$ → C <sub>2</sub> H + <u>H</u>	0.26	VUV-LIF, ABS	1.35 × 10 <sup>-19</sup>
CCl <sub>4</sub>	CCl <sub>4</sub> + h $\nu$ → nCl + CCl <sub>3</sub> → Cl + SiH <sub>4</sub> → <u>SiH<sub>3</sub></u> + <u>HCl</u>	$\Phi_{Cl}$ = 1.2 $\Phi_{SiH_3}$ = 0.9	EI-MS	[Yield of SiH <sub>3</sub> at 12mJ/cm <sup>2</sup> ; (SiH <sub>3</sub> )/(CCl <sub>4</sub> ) = 0.0037]
H <sub>2</sub> S	H <sub>2</sub> S + h $\nu$ → HS + <u>H</u>	0.90 ± 0.24	VUV-LIF, ABS	1 × 10 <sup>-17</sup>
N <sub>2</sub> O	N <sub>2</sub> O + h $\nu$ → N <sub>2</sub> + O( <sup>1</sup> D) O( <sup>1</sup> D) + N <sub>2</sub> O → <u>NO</u> + <u>NO</u> (k <sub>2a</sub> ) → N <sub>2</sub> + O <sub>2</sub> (k <sub>2b</sub> )	$\Phi_O$ = 1 $\Phi_{NO}$ = (*1) 1.05 (T=316K) 0.79 (T=433K)	EI-MS	9.5 × 10 <sup>-20</sup> (T=313K) 1.3 × 10 <sup>-19</sup> (T=433K)
HNCO	HNCO + h $\nu$ → <u>H</u> + NCO → NH( <sup>1</sup> Δ) + CO NH( <sup>1</sup> Δ) + H <sub>2</sub> → <u>H</u> + NH <sub>2</sub>	$\Phi_H$ = 0.08 $\Phi_{NH}$ = 0.11	VUV-LIF, ABS	4.7 × 10 <sup>-19</sup>
CH <sub>3</sub> OH	CH <sub>3</sub> OH + h $\nu$ → CH <sub>3</sub> O + <u>H</u> → CH <sub>2</sub> OH + <u>H</u> CH <sub>3</sub> OD + h $\nu$ → CH <sub>3</sub> O + <u>D</u> CH <sub>2</sub> OD + <u>H</u>	0.56 $\Phi_D$ = 0.49 (*2) $\Phi_H$ = 0.07	VUV-LIF, ABS	3.0 × 10 <sup>-19</sup>