A NEW METHOD TO MEASURE WATER VAPOR CONTENT OF THE POLAR MIDDLE ATMOSPHERE USING PHOTOCHEMICAL REACTION " $H_2O + h\nu(121.6 \text{ nm}) \rightarrow OH^* + H$ "

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Abstract: A method of water vapor measurement in the upper troposphere and the stratosphere of the polar region is described. This technique is due to the photochemical reactions, $H_2O+h\nu(Lyman-alpha line)\rightarrow OH(A^2\Sigma^+)+H$, $OH(A^2\Sigma^+)\rightarrow OH(X^2\Pi)+h\nu(309 \text{ nm})$, and has several advantages such as fast response and high sensitivity, besides being relatively free from contamination.

Results of laboratory experiments suggest that this method is possibly very useful for monitoring the content of water vapor under a very dry atmospheric condition like the polar middle atmosphere.

1. Introduction

The water vapor of the polar middle atmosphere plays an important role in various aeronomical processes; for example, photochemistry of the stratosphere or the mesosphere, clustering of water molecules around ion of ionospheric D region, airglow from OH radical, formation of noctilucent cloud particles, behavior of the socalled "Stratospheric Cist" and so on. These geophysically interesting problems unfortunately remain to be solved owing to the lack of sufficient measurements on water vapor distribution and its variation in the polar middle atmosphere. Even the measurements of water vapor concentration in the stratosphere or the mesosphere of lower and middle latitudinal regions are very limited, and large uncertainties exist in the obtained data (*e.g.*, review by HARRIES, 1976). At the present time, it is difficult, if not impossible, to establish a consistent picture concerning the natural variation of water vapor concentration in the middle atmosphere, and of course more measurements are necessary. From the viewpoint of transportation of H₂O vapor in the stratosphere, it has been speculated that the polar stratosphere functions as an active sink, and a large-scale transportation from the equatorial region to the polar region

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is existing (GIRARD *et al.*, 1978), and additionally the transportations of ozone and aerosol particles of the stratosphere on a global scale are occurring. Therefore, measurements of water vapor in the polar stratosphere and the mesosphere will provide very useful information for understanding the transportation mechanism of not only stratospheric water vapor but also stratospheric ozone or aerosol particles.

Previously, TERENIN and NEUJMIN (1934) showed that when H_2O is illuminated at wavelengths less than 137 nm, it dissociates as follows,

$$H_2O + h\nu \to OH(A^2\Sigma^+) + H(^2S)$$
⁽¹⁾

and excited state $OH(A^2\Sigma^+)$ radicals are emitted at around 309 nm.

Recently KLEY and STONE (1978) have pointed out that this fluorescence effect of excited state radical OH($A^2\Sigma^+$) is useful to the measurement of the water vapor concentration under the atmospheric condition where the mixing ratio of water vapor is very low, for example, the stratosphere or the mesosphere, and after that KLEY *et al.* (1979) have presented the measurement of the stratospheric water vapor mixing ratio using this fluorescence effect of OH radical produced through the photodissociation reaction (1). As pointed out by KLEY and STONE (1978) and KLEY *et al.* (1979), this method has essentially two advantages, namely rapid response and high sensitivity, which are very useful for constructing a hygrometer of balloon-borne type.

We have continued experimenting on this technique in order to work out a measurement system of water vapor concentration for about two years. We should like to present the experimental results of the fluorescence effect technique and discuss its usage.

2. Theory and Instrumentation for Water Vapor Measurement

2.1. Principle of measurement system

At a wavelength of 121.6 nm (Lyman-alpha line), the absorption cross section of water vapor is abont 10^{-17} cm², and nitrogen molecule which is a major component in the lower or middle atmosphere of the earth is completely transparent to this line. This wavelength and its vicinity are so-called "oxygen window", and the mixing ratio of water vapor in the atmosphere is very effective to the attenuation of Ly- α line intensity due to absorption (see Fig. 1).

This absorption effect by water vapor has been applied for monitoring the water vapor content in the lower atmosphere worldwidely.

Figure 2 illustrates the schema showing the principle of the water vapor measurement system.

The excited state radical OH($A^{2}\Sigma^{+}$) is emitted at around 309 nm according to,

$$OH(A^{2}\Sigma^{+}) \rightarrow OH(X^{2}\Pi) + h\nu : A$$
 (2)

and the following deactivating reaction occurs simultaneously under the atmospheric



Fig. 1. Absorption cross section of oxygen and water vapor versus wavelength (after BERTAUX and DELANNOY, 1978).



Fig. 2. Schema of the principle of the instrument.

conditions,

$$OH(A^{2}\Sigma^{+}) + M(M = O_{2} \text{ or } N_{2}) \rightarrow products : k_{M},$$
 (3)

where

- A: the transition probability,
- k_{M} : the rate constant of quenching reaction.

The values of A and k_M are listed in Table 1.

Ouenching rate constant		
k_{0}	8.3 $\times 10^{-11}$ cm ³ s ⁻¹	(Homer and Hurle, 1970)
$k_{N_2}^{-2}$	$1.1 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$	(Homer and Hurle, 1970)
*k _{air}	2.8 ×10 ⁻¹¹ cm ³ s ⁻¹	(KLEY and STONE, 1978)
Transition probability		
$A_{(v=0)}$	$1.26 imes 10^6 \mathrm{s}^{-1}$	(CROSLEY and LENGEL, 1975)
	1.72×10 ⁶ s ⁻¹	(German <i>et al.</i> , 1973)

Table 1. Quenching rate constant and transition probability.

* k_{air} is given by following equation in the troposphere and stratosphere, $k_{air} = k_{02}[m/(m+1)] + k_{N2}[1/(m+1)]$

The life times of reactions (2) and (3) are so short that it can be assumed that the excited state OH radical is chemically in equilibrium with H_2O vapor concentration. This equilibrium concentration of OH radical is given by,

$$[OH(A^{2}\Sigma^{+})] = [H_{2}O]Je/(A + \sum_{M=O_{2},N_{2}} k_{M}[M]), \qquad (4)$$

where

- J: the photodissociation rate constant of reaction (1),
- e: the quantum yield of reaction (1).

The intensity of fluorescence light from excited state radical $OH(A^2\Sigma^+)$ is given by,

$$I = [OH(A^2 \Sigma^+)]A .$$
⁽⁵⁾

Considering the values of parameters listed in Table 1, it can be easily found that $\sum_{M=O_2, N_2} k_M[M] \gg A$ is satisfied under the atmospheric condition of the stratosphere and the troposphere, then eq. (5) is rewritten in the following form,

$$I = [H_2 O] JeA / (\sum_{M=O_2, N_2} k_M[M]).$$
(6)

According to many investigations, the ratio of $[O_2]/[N_2]$ is constant up to the upper mesosphere, then we can again rewrite eq. (5) as follows by using the value of m (= $[O_2]/[N_2]$),

$$I = [H_2O] JeA/(k_{O_2}[m/(m+1)] + k_{N_2}[1/(m+1)])[air],$$
(7)

where

[air]: number density of air molecule, and given by $[air] = [N_2] + [O_2]$.

This equation shows that it is possible to measure directly the mixing ratio of water vapor. In eq. (7), photodissociation rate J is given by the following equation,

$$J = \int F(\lambda) \sigma_{\mathrm{H}_{2^0}}(\lambda) \mathrm{d}\lambda , \qquad (8)$$

where

 $F(\lambda)$: the flux of ultraviolet light in the fluorescence region,

 $\sigma_{\rm H_{g0}}(\lambda)$: the absorption cross section of water vapor at wavelength = λ .

The flux of ultraviolet light at a distance l_1 from the UV light source is given by,

$$F_{1}(\lambda) = F_{0}(\lambda) \exp[-(\sigma_{H_{2}O}(\lambda)[H_{2}O] + \sigma_{O_{2}}(\lambda)[O_{2}])l_{1}], \qquad (9)$$

where

 $F_0(\lambda)$: the flux of UV radiation at the light source,

 $\sigma_{O_2}(\lambda)$: the absorption cross section of O₂ molecule.

The photon flux measured by "detector 2" in Fig. 2 is

$$F_{2}(\lambda) = F_{0}(\lambda) \exp\left[-(\sigma_{\mathrm{H}_{0}0}(\lambda)[\mathrm{H}_{2}\mathrm{O}] + \sigma_{\mathrm{O}_{0}}(\lambda)[\mathrm{O}_{2}])l_{2}\right].$$
(10)

Under the condition where the concentration of water vapor is enough to cause the attenuation of light due to absorption, the value $F_2(\lambda)/F_1(\lambda)$ determined by eq. (10) becomes detectable, then we can easily estimate the water vapor content as described in the initial part of this subsection.

2.2. Instrumentation

Figure 3, 4 and 5 are block diagrams of the instrument used here. This instrument was designed for tentative use in the laboratory to check its feasibility. As shown in Fig. 3, the sensing unit of the instrument is composed of a hydrogen lamp, a nitric oxide (NO) ion chamber, a photomultiplier tube, and a chamber for humidity measurement. The hydrogen lamp is the source of Lyman-alpha (121.6 nm) light, and the NO chamber is used for *in-situ* calibration of the output power from the photomultiplier and for the detection of the attenuation of the Ly- α light due to absorption by H₂O or O₂ in the chamber. The photomultiplier tube for the measurement of emission from excited OH is aligned at right angles to the hydrogen lamp and the NO chamber. The combination of the hydrogen lamp and the NO chamber can



Fig. 3. Sensing unit of the instrument.

be used as a Ly- α hygrometer which has been developed as a fast responding humidity sensor in the lower troposphere as already described in Subsection 2.1 (TILLMAN, 1965; RANDALL *et al.*, 1965; BUCK, 1976, 1979). The distance L₂ denoted in Fig. 3 can be changed from 0.3 cm to 9.3 cm at 0.5 cm step. In order to measure the water vapor concentration in a rather dry atmosphere such as the middle atmosphere, the distance L₂ should be made relatively long. The distances L₁ and L₃ are 2 cm and 7.7 cm respectively, but they are properly changeable. The chamber having inlet and outlet of air is made of plastics coated with optical black paint to intercept the light from the outside of the chamber or to avoid reflection of light from the source light on the internal surface of the chamber. Air is introduced into this chamber with a pump, and humidity is measured by two different methods, 1) the absorption effect of Ly- α source light, and 2) the fluorescence effect of excited state radical OH.

The hydrogen lamp and the NO chamber adopted in this instrument are of the same type as those used in the NCAR Lyman-alpha hygrometer (BUCK, 1979): the hydrogen lamp (GT202M) and the NO chamber (GT203D) were manufactured by Glass Technologists Co. (U.S.A.) (see Table 2). The hydrogen lamp is a DC-excited cold-cathode glow discharge lamp. Hydrogen is filled in a Pyrex cylinder at a pressure of 800 Pa, and the lamp is sealed off with a MgF₂ window whose area is about 0.64 cm². The lamp is operated with voltage of about -320 V, and hydrogen glow discharge between two electrodes emits light of Ly- α line (121.6 nm). The disadvantage of this lamp is that its life time is not very long (several hundred hours) and there remain spectral lines other than Ly- α line in the emission spectra. The NO chamber is made of a Pyrex cylinder and is filled with nitric oxide at a pressure of 1600 Pa. The NO chamber is operated with voltage of about -70 V. When UV lights of wavelength from 115 nm to 135 nm enter the NO chamber through the

Item	Manufacturer	Model
Hydrogen lamp	Glass Technologists 700 Holly Drive North Route 10 Annapolis, MD. 21401 U.S.A.	GT202M
NO ion chamber	Glass Technologists	GT203D
Electrometer	Teledyne Philbrick	1035
Logarithmic operator	Teledyne Philbrick	4358
High voltage power supply	Mizojiri Optical Co.	PH-7B
Photomultiplier tube	Hamamatsu TV Co.	R585
Pre-amplifier for photomultiplier	Hamamatsu TV Co.	C716
Photon counter	Hamamatsu TV Co.	C1230

Table 2. Parts list of the instrument.

MgF₂ window, the NO gas filling the NO chamber is ionized, and this yields an electric current between two electrodes. By measuring the intensity of this current, we are able to know the intensity of Ly- α light entering the NO chamber. Figure 4 is a block diagram of the circuit for measuring the attenuation of Ly- α light through the sensing path in the chamber. As was mentioned previously, this part of the instrument was used as a Lyman-alpha hygrometer, and the design of the circuit presented here is essentially the same as the conventional Lyman-alpha hygrometer (BUCK, 1979). A hygrometer of this type is very useful for the measurements of the water vapor content of the lower atmosphere, but is not good for detecting the humidity of the middle atmosphere since the middle atmosphere does not contain a large amount of water vapor, so that the decrease of light intensity of Ly- α line due to



Fig. 4. Block diagram of the circuit (part of the instrument so called Lyman-alpha hygrometer).



Fig. 5. Block diagram of part of the instrument measuring OH fluorescence.

the absorption by water vapor can be hardly detected.

The most important part of this instrument is the detector of fluorescence from excited state OH radical produced through photodissociation reaction of H₂O. Intensity of the OH fluorescence is so weak that it is required to use the photon counting technique. The photomultiplier tube used in this instrument is the model R585 produced by Hamamatsu Television Co. It has a bialkali cathode and a quartz window of 0.4 cm^2 in area, and it is sensitive in the wavelength range of 160 nm-650 nm. The photomultiplier used here is suitable for the photon counting method, and its background counting rate is suppressed to 5 cps (counts per second) at 20°C. In front of the photomultiplier is an interference filter whose peak wavelength, halfvalue band width, and transmission are 306.5 nm, 17.5 nm and 17% respectively. Signal from the photomultiplier is amplified by pre-amplifier (Hamamatsu C716), and is fed to the photon counter (Hamamatsu C1230). The background counts (dark counts) are eliminated from the signal by a discriminator, and the counting rate corresponding to the photon flux entering the photomultiplier is displayed in the front panel of the photon counter or in the output to the recorder. The maximum counting rate of the photon counter is 10⁷ cps.

3. The Results of Laboratory Experiment

As described in Subsection 2.1, the photon number measured by the photomultiplier is proportional to the volume mixing ratio of water vapor in the air.

In practical use the instrument is operated in a relatively dry condition. To obtain various dry conditions in the chamber, we let the air in the chamber circulate between the chamber and the bottle containing P_2O_5 which acts as a desicant, or we introduced extremely dry standard air filling up a bomb into the chamber (see Fig. 6a and 6b). Humidity in the chamber was measured also by using the NO chamber whose output signal is previously well calibrated with a Humicap Hygrometer manufactured by Vaisala Oy and a thermocouple thermometer. Figure 7 is an example of our test (see Table 3). The distances L_1 , L_2 and L_3 of the sensing unit (see Fig. 3) were 2 cm, 3.8 cm and 7.7 cm respectively. The lamp current was -0.90 mA, and supply voltage of the photomultiplier was -750 V. Although we did not let the discriminator operate in this test, the background counting rate was less than 60 cps. Since the output of the NO chamber is a function of absolute humidity, we convert this to the volume mixing ratio assuming air temperature=288.16 K, and air pressure=101.3 kPa.

As shown in Fig. 7, in a dry region (water vapor mixing ratio < 800 ppm V), the counting rate of the photomultiplier is proportional to the volume mixing ratio of H₂O vapor, and the sensitivity of the instrument is about 10 cps/ppm V. As the volume mixing ratio increases or exceeds about 800 ppm V, the relation between the photon counting rate and the volume mixing ratio shows a non-linear feature,



Fig. 6. Schematic diagram of laboratory test (a: using P_2O_5 , b: using gas in bomb).



Fig. 7. Output counting rate versus water vapor content in the air. To make dry condition dry standard air in bomb was used. Condition for the test is presented in Table 3.

Item	Condition	
Distance between sensing components		
Lı	2 cm	
L_2	3.8 cm	
L_3	7.7 cm	
Hydrogen lamp current	$-0.90 \mathrm{mA}$	
Supply voltage of the photomultiplier	-750 V	
Discriminator	Off	
Gas supplied from bomb	N_2 or $N_2 + O_2$	

Table 3. Condition for laboratory tests.

and furthermore in a region where the volume mixing ratio exceeds 2000 ppm V, the counting rate gradually decreases. These facts are possibly caused by the following processes:

1) In a relatively "moist" atmosphere condition, most of photons emitted from the source light do not reach the viewing area of the photomultiplier due to strong absorption by water vapor, so that the production rate of excited state OH is extremely small. Under such condition, the counting rate of fluorescence does not show the proportional relation to the volume mixing ratio of H_2O derived from the theoretical treatment (eq. (7)).

2) Photomultiplier becomes unable to respond since the water vapor content is rather large, and then the intensity of OH radical emission becomes too strong. Another point in this figure to be mentioned is that the extrapolated value of the counting rate corresponding to 0 ppm V is relatively large. This is probably because



Fig. 8. Same as Fig. 7 except that results of the test using dry nitrogen is added (•: dry standard air, o: dry nitrogen).

the hydrogen lamp emits extraneous lights other than Ly- α light (BUCK, 1977). Practically the hydrogen lamp used here is emitting visible lights. If the lamp emits lights whose wavelength is around 309 nm, these lights may be scattered by the internal surface of the chamber or by aerosol particles floating in the air, and they may contribute to the counting rate of the photomultiplier.

Fig. 8 is another example of tests in the same condition except that dry nitrogen was used instead of dry standard air. In this case the results show a similar tendency as the one when dry standard air was used. However, the counting rate exhibits remarkable increase and decrease as the volume mixing ratio of H_2O changes. And sensitivity of the instrument in a dry region increases to about 60 cps/ppm V. This is partly due to the decrease of Ly- α light through the absorption by molecular oxygen. And another reason is that the rate of quenching of OH* by nitrogen is about half of that by air, then OH fluorescence is more intense in a nitrogen atmosphere (KLEY and STONE, 1978).

4. Discussion and Conclusion

There are few measurements on the water vapor content of the upper troposphere, the stratosphere and the mesosphere, since technically it is impossible to detect water vapor with traditional method such as dew-point hygrometer under these very dry atmospheric conditions. In the near future, the usage of aircraft for monitoring various atmospheric parameters in the upper troposphere and the stratosphere would become very popular. Under such situation, the method having not only high sensitivity but also fast response is desired.

The technique presented here is quite advantageous for measuring the water vapor content under a very dry atmospheric condition and for mounting the instrument on aircraft or balloon, but it is not a fully established one. Some very limited scientific groups have been developing this technique, but the technique is not used generally yet. Development of a new method is a very difficult and costly work, but we must achieve it in order to make clear the behaviour of water vapor of the polar middle atmosphere. In addition to this, this method of instantaneously measuring very low humidity promises many new opportunities in the fields of not only meteorology but also physics and chemistry, and the technical information described here must be useful to the researchers who are willing to measure very low humidity.

In this experiment, we could confirm that the measurements of the water vapor content by using the fluorescence effect of excited state $OH(A^2\Sigma^+)$ radical produced through photodissociation, $H_2O + h\nu(Ly-\alpha \text{ line})$.

 $OH(A^2\Sigma^+)$ +H, had the following advantages in comparison with previous instruments such as dew-point hygrometer, hair hygrometer and so on;

1) fast response (probably of 10 ms order at the level of water vapor content=1000 ppm V),

- 2) high sensitivity (800 ppm V-50 ppm V),
- 3) freedom from contamination (relatively).

Ly- α line can be absorbed by not only H₂O, NO or O₂ but also other various gases in the atmosphere, that is, HNO₂, CO₂, CH₄ and H₂O₂. Additionally photodissociation of H₂O₂ by UV light can produce an excited state OH($A^2\Sigma^+$) radical. However, the mixing ratios of these gases in the upper troposphere or the stratosphere, and quantum yields in photodissociation at wavelength of 121.6 nm show that these effects will not have a real influence.

Geometrical condition of the instrument, particularly lengths l_1 and l_2 , and the view of the photomultiplier would affect seriously the dynamic range of measurement. The choice presented in this experiment is not a unique one.

We felt that in order to adopt completely this technique to the monitoring of the water vapor content in the polar middle atmosphere, further improvements, as follows, must be made:

1) the purity of source light (in practical use, it is better to use the hydrogen lamp containing uranium hydride, UH_3),

- 2) the monitoring on the change of source light intensity,
- 3) the test on the quality of material from which the chamber is made,
- 4) the protection against the stray light or electronic noise.

We should like to establish an accurate and simple method of calibration under an extremely dry condition, and construct a practical instrument (aircraft- or balloon-borne type) in the near future.

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Appendix

Photographs showing the instrument and structure of lamps (hydrogen lamp and NO ion chamber) are presented as appendix.



Fig. A-1. Sensing unit.

a. Hydrogen lamp (inside). b. NO ion chamber (inside), electrometer (inside), pre-amplifier (inside). c. Photomultiplier tube (inside). d. Pre-amplifier for photomutilplier tube. e. Chamber for humidity measurements.



Fig. A-2. Control chasis.

a. Control chasis for "Lyman-alpha hygrometer". b. High voltage power supply. c. Photon counter.



Fig. A-3. Hydrogen lamp (cited from BUCK, 1979).



Fig. A-4. Nitric oxide ion chamber (cited from BUCK, 1979).