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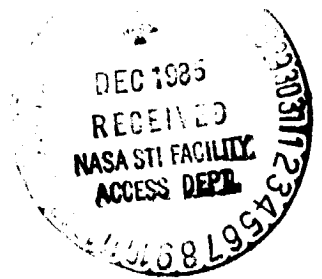
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December 12, 1985

Annual Technical Report for Grant No. NAGW-661

Covering the period from December 1, 1984 to November 30, 1985

Measurements of HO$_2$ Chemical Kinetics with a New Detection Method

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TABLE OF CONTENTS

I. INTRODUCTION

This report describes the results obtained in the period from December 1, 1984 to November 30, 1985 for the research program currently supported by NASA under Grant No. NAGW-661 basic. In this research program, HO_2 was detected by the OH(A-X) photofragment from dissociative excitation of HO_2 at 147 nm. This detection method was applied to measure the reaction rate constant of $HO_2 + O_3$. This reaction rate constant is needed for the understanding of stratospheric chemistry.

Since Cl_2 was used in the flow system, photoexcitation of Cl_2 may produce fluorescence to interfere with our measurements. Thus, the photoexcitation process of Cl_2 in the vacuum ultraviolet region was also examined in this research period using synchrotron radiation as a light source. The research results are summarized below.

II. RESEARCH ACCOMPLISHED

A. Experimental Apparatus

A discharge-flow-tube apparatus has been constructed in the current funding period. The schematic diagram for the apparatus is shown in Fig. 1. The flow tube consists of a large tube of 4.8 cm ID and 60 cm long, and a movable injector of 1 cm ID and 70 cm long. (The large tube of 4.8 ID was later changed to 2.3 cm to check the effect of walls on the reaction rate measurement). Inside the injector there is a small teflon tube of 2 mm ID. O_3 was produced by a high voltage a.c. discharge of O_2 and stored in two silica gel traps attached to the flow tube.
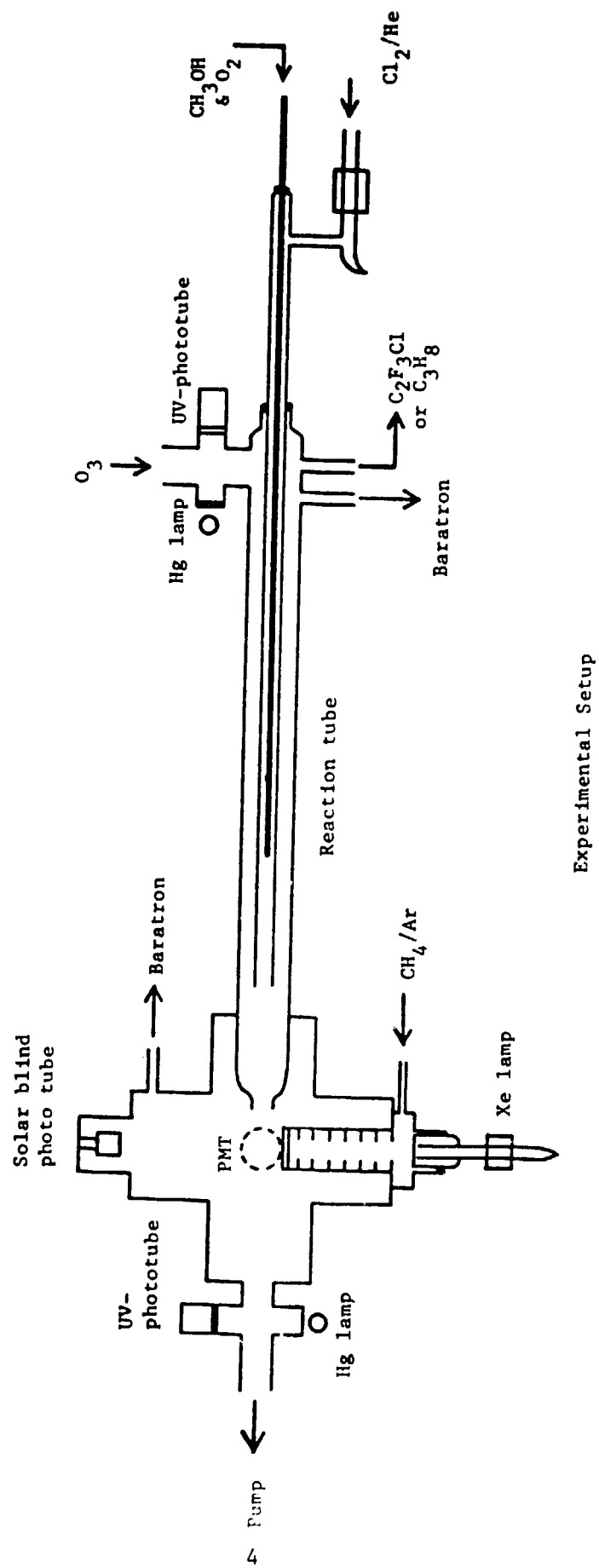
CH₃OH & O₂

Cl₂/He

UV-phototube

O₃

Hg lamp

C₂F₃Cl or C₃H₈

Baratron

Reaction tube

Solar blind photo tube

Baratron

CH₄/Ar

UV-phototube

PMT

Xe lamp

Hg lamp

Pump

4

Experimental Setup

Fig. 1

The O_3 concentrations were monitored at two positions before and after the flow tube. HO_2 in a gas cell was detected by a Xe resonance light at 147 nm. The gas cell was a six-way cross of 3" OD which was made of stainless steel.
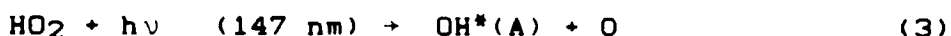
B. Production and Detection of HO_2

HO_2 was produced by microwave discharge of a trace of Cl_2 in He, which then reacted with CH_3OH and O_2 by

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \tag{1}$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \tag{2}$$

The measurements of gas pressures and the control of gas flow rates has been described in detail in the Semiannual Report.

HO_2 was detected by the OH(A-X) emission produced from photodissociative excitation of HO_2 by a Xe resonance light at 147 nm,

$$HO_2 + h\nu \quad (147 \text{ nm}) \rightarrow OH^*(A) + O \tag{3}$$

$$OH^*(A) \rightarrow OH(X) + h\nu \ (306\text{-}320 \text{ nm}) \tag{4}$$

The attenuation of the light source and the quenching of $OH^*(A)$ by the gases in the gas cell were carefully examined, which were described in detail in the Semiannual Report.

C. Reaction Rate Constant of $HO_2 + O_3$

The reaction rate constant of $HO_2 + O_3$ has been measured by Zahniser and Howard [J. Chem. Phys. 73, 1620 (1980)] to be 2×10^{-15} cm^3/s,

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{5}$$

OH will react with O_3 to form HO_2 again,

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{6}$$

with a reaction rate constant of 6.5×10^{-14} cm^3/s. In order to measure the rate constant of reaction (5), the OH radicals need

to be scavenged. C_2F_3Cl and C_3H_8 were used as the OH scavengers
in our experiments,

$$OH + C_2F_3Cl \rightarrow products \quad k_7 = 6 \times 10^{-12} \ cm^3/s \quad (7)$$

$$OH + C_3H_8 \rightarrow products \quad k_8 = 1.1 \times 10^{-12} \ cm^3/s \quad (8)$$

For $[O_3]$ varied in the 30-100 mtorr range in our
experiments, 100 mtorr of C_2F_3Cl or 200 mtorr of C_3H_8 will
effectively eliminate OH in the system.   Thus, the effect of OH
on the $HO_2 + O_3$ reaction rate measurement is minimized.

At each $[O_3]$, the psuedo-first-order-decay rate, K, of HO_2
was measured by the relative HO_2 concentration in the gas cell as
a function of the $HO_2 + O_3$ reaction time by changing the HO_2 flow
distance in the flow tube.   The K values measured at various $[O_3]$
are shown in Fig.   2,   where (200-250) mtorr of C_3H_8 was used   as
the OH scavenger.   The reaction rate constant determined from the
plot is $(2.1 \pm 0.5) \times 10^{-15} \ cm^3/s$.   This result is consistent with
the value of Zahniser and Howard of $2.0 \times 10^{-15} \ cm^3/s$.

We   also measured the $HO_2 + O_3$ reaction rate constant   using
C_2F_3Cl as   the   OH scavenger.   This molecule has been   used   by
Zahniser and Howard in their $HO_2 + O_3$ kinetics measurements.   The
psuedo-first-order-decay   rates of HO_2 as a function of $[O_3]$ are
shown in Fig.   3,   where about 120 mtorr of C_2F_3Cl was used as the
OH scavenger.   The reaction rate constant determined   from   the
plot is $(1.5 \pm 0.4) \times 10^{-15} \ cm^3/s$.   In this measurement, we observed
that C_2F_3Cl produced fluorescence in the UV region when it   was
excited by the 147 nm light.   Although the fluorescence intensity
was relatively   small when a narrow band filter $(310 \pm 10 \ nm)$ was
used to isolate the emission band,   the fluorescence may somewhat

Fig. 2

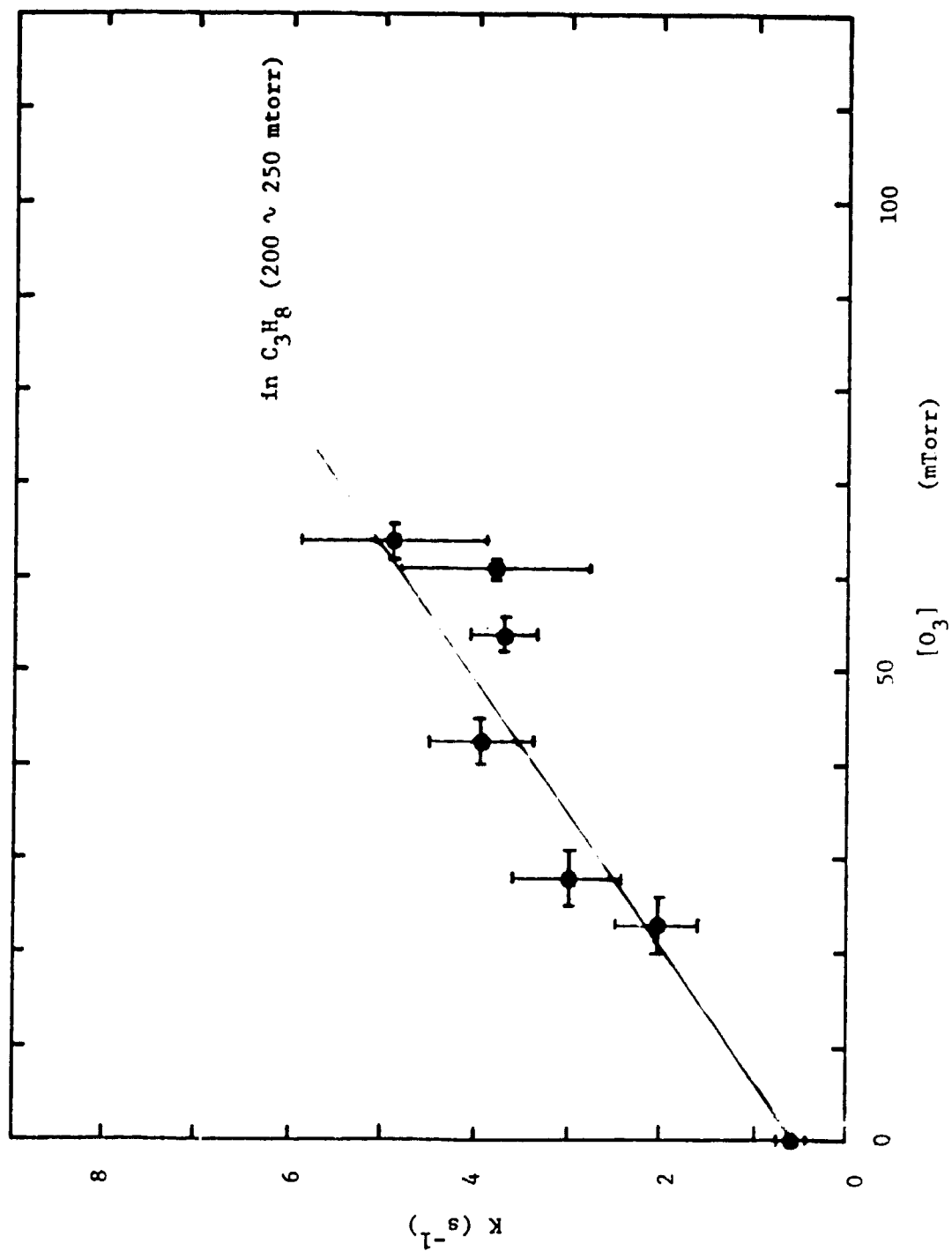In C_3H_8 (200 ∿ 250 mtorr)

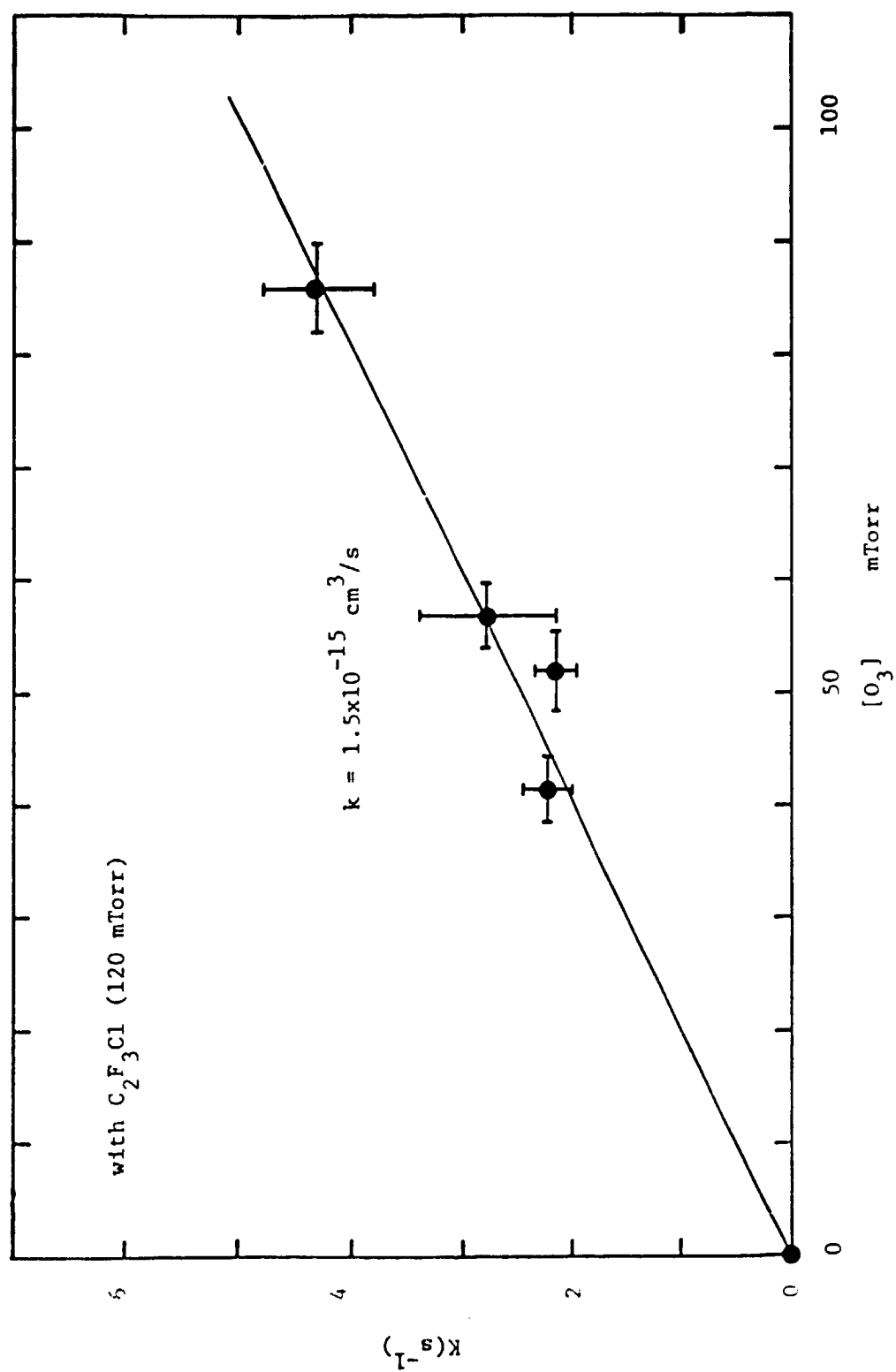$[O_3]$ (mTorr)

K (s^{-1})

7

Fig. 3

8

disturb the observed signal. The fluorescence intensity from C_2F_3Cl has been corrected in the decay rate measurement.

In order to check the effect of walls on the measured reaction rate constant, we changed the flow tube size from 4.8 cm ID to 2.3 cm ID. The psuedo-first-order-decay rates of HO_2 measured with this small flow tube as a function of $[O_3]$ are shown in Fig. 4, where C_2F_3Cl was used as the OH scavenger. The reaction rate constant determined from the plot is $(1.7 \pm 0.2) \times 10^{-15}$ cm^3/s. This result will be checked again using C_3H_8 as the OH scavenger.

From the above results, the rate constant of the $HO_2 + O_3$ reaction (averaged over the data points) is $(1.8 \pm 0.3) \times 10^{-15}$ cm^3/s. We will take more data to reduce the experimental uncertainty, and then report the results in a scientific journal.

D. Photoexcitation Process of Cl_2

Cl_2 was used in the flow system to produce Cl atom that finally made HO_2. We observed that Cl_2 has a weak ultraviolet fluorescence when excited at 147 nm. It is interesting to study the fluorescence process, because it is useful to assess the interference of the Cl_2 fluorescence to our kinetics measurements. In addition, the photodissociation process of Cl_2 is also of interest in the study of the upper atmospheric photochemistry. The photodissociation of Cl_2 by vacuum ultraviolet radiation in the upper atmosphere is a source of Cl atom. Based on these needs, we studied the photoexcitation process of Cl_2 using synchrotron radiation in the 105-200 nm region. The results are summarized in a paper entitled "Quantitative VUV Spectroscopy of Cl_2" which is attached as an
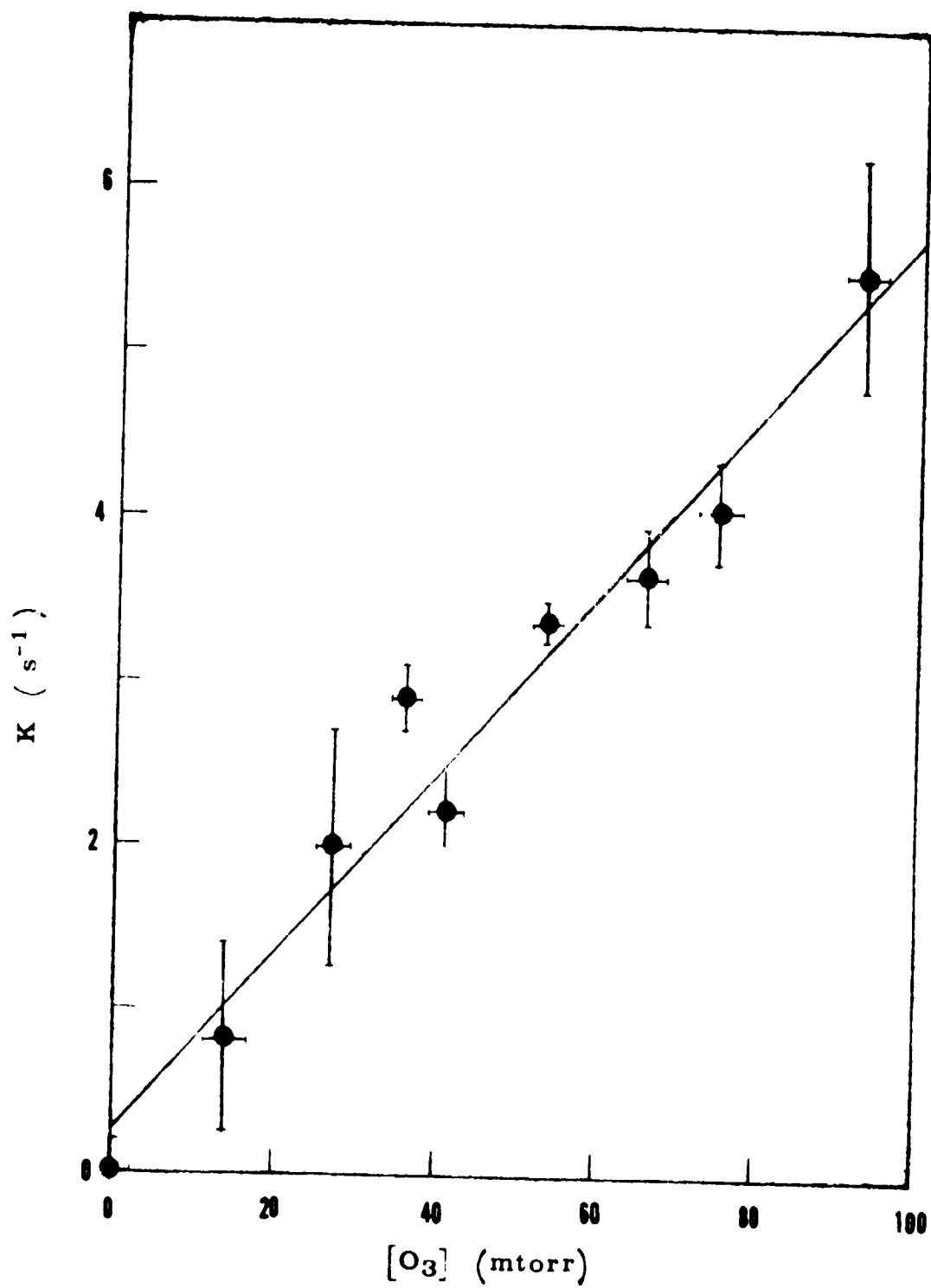
Fig. 4

Appendix. This paper has been submitted to the Journal of Chemical Physics for publication.

The absorption of Cl_2 in the VUV region is dominated by strong discrete structures. 147 nm is at the tail of the absorption band of the $1^1\Sigma^+$ Rydberg state. Both absorption and fluorescence cross sections of Cl_2 at 147 nm are quite small, thus, the fluorescence does not impose a serious interference to our kinetics measurements. The minor effect caused by the fluorescence from the photoexcitation of Cl_2 was corrected in the data shown in Figs. 2-4.

III. CUMULATIVE PUBLICATIONS AND PRESENTATIONS

Our preliminary works have been reported in scientific community as listed below:

1.   M. Suto and L. C. Lee, "Photofragment Emission from HO_2 and its Application to the HO_2 Kinetics Study", presented at the Informal Atmospheric Kinetics Meeting, Jet Propulsion Laboratory, Pasadena, CA, Jan. 18, 1985.

2.   M. Suto, "Study of the HO_2 + O_3 Reaction by Detecting HO_2 from Photofragment Emission", Seminar presented to the Naval Research Laboratory, Washington D. C., June 14, 1985.

3.   L. C. Lee and M. Suto, "Photoexcitation Process of Cl_2 in VUV", presented at the 1985 SRC Users Group Meeting, Madison, Wisconsin, Oct. 21-22, 1985.

4.   L. C. Lee, M. Suto and K. Y. Tang, "Quantitative VUV Spectroscopy of Cl_2", submitted to J. Chem. Phys. (1985).

IV. APPENDIX

"Quantitative VUV Spectroscopy of Cl_2"

Quantitative VUV Spectroscopy of Cl$_2$

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ABSTRACT

The photoabsorption and fluorescence cross sections of Cl$_2$ were measured in the 105-145 nm region using synchrotron radiation as a light source. The oscillator strengths for the major absorption bands are calculated from the measured absorption cross sections. The measured oscillator strengths for the $2^3\Pi_u$ and $2^1\Pi_u \leftarrow X^1\Sigma_g^+$ transitions agree quite well with the theoretical values. The absorption spectrum was analyzed in accord with the excited electronic states calculated by Peyerimhoff and Buenker (1981). The Rydberg series converging to the first and second ionization potentials were classified. The vibrational levels of the $2^1\Sigma_u^+$ ionic state were determined up to $v' = 15$ from the fluorescence excitation spectrum. It was observed that a band with peak at 108.3 nm produces VUV fluorescence, but it produces UV fluorescence only by a collisional excitation process.

I. INTRODUCTION

The electronic transitions of chlorine molecule in the vacuum ultraviolet (VUV) region have been subject to extensive investigations.[1-4] Lee and Walsh[1] observed the absorption spectrum in the 107-210 nm region with a 1-m vacuum spectrograph. The absorption bands for wavelengths longer than 130 nm were assigned to possible electronic states in accord with molecular-orbital theory. However, the absorption bands at wavelengths shorter than 130 nm were so complicated that they were not analyzed. Iczkowski et al.[2] revisited the absorption spectrum in the 110-135 nm region in order to clarify the possible impurity (HCl) contamination of the Cl_2 spectrum observed by Lee and Walsh[1]. A Rydberg series coverging to the first ionization potential at 11.47 eV was found.[2]

The rotationally resolved absorption spectrum was observed and analyzed in the 133-145 nm region by Douglas[3] using a 10.7 m vacuum spectrograph. An ionic state, $1^1\Sigma_u^+$, was determined from the analysis. The absorption spectrum in the 107-130 nm region has been taken by Douglas but it was not analyzed because of complexity. Recently, Moeller et al.[4] studied the absorption spectrum of Cl_2 in the 120-140 nm region using synchrotron radiation. Fluorescence from the $1^1\Sigma_u^+$ state was observed and dispersed. The absorption spectrum was interpreted with the potential curves calculated by Peyerimhoff and Buenker[5]. The nature of the electronic transition of the absorption spectrum in the 130-145 nm region is now well understood,[1-5] although the transitions in the 105-130 nm region are still not clear.

The absolute absorption and fluorescence cross sections of Cl_2 in the VUV region are reported in this paper. These data are useful for understanding the nature of electronic states in the short wavelength region. The quantitative data are also needed in several application areas. For example, Cl_2 has been used in our laboratory for the study of HO_2 kinetics.[6] The fluorescence cross section of Cl_2 is needed for examining the effect of Cl_2 fluorescence on the kinetics measurement. Cl_2 is also generally used in the chemical etching of semiconductor materials and in the rare gas-excimer laser. The quantitative photoexcitation data of Cl_2 are useful for understanding the role its plays in various environments. In addition to these pracitcal applications, the oscillator strengths determined from the measured absorption cross sections are useful for comparison with the results of ab initio calculations.[7]

II. EXPERIMENTAL

The experimental set-up for the current measurement has been described in a previous paper.[8] In brief, synchrotron radiation produced from the electron storage ring at the University of Wisconsin was dispersed by a 1-m Seya vacuum monochromator. The optical path of the absorption cell was 39.2 cm. The VUV light source was converted into UV light by sodium salicylate coated outside a LiF window and then detected by a photomultiplier tube (PMT). The fluorescence was monitored by a PMT (EMI 9558QB) in the UV-visible region and a solar blind PMT (EMI, CsI cathode) in the VUV region. The UV and VUV fluorescences were observed in directions orthogonal to the light beam. The UV fluorescence

cross section was calibrated by comparing the Cl_2 fluorescence intensity with the OH(A-X) fluorescence from photodissociation of H_2O, for which the fluorescence cross section is known.[8] The fluorescence quantum yield is then determined from the ratio of fluorescence cross section to absorption cross section. The absolute cross section for the production of VUV fluorescence was calibrated by comparing the observed Cl_2 fluorescence intensity with the CO resonance fluorescence intensity, for which the CO fluorescence cross section is assumed to be equal to the CO absorption cross section.

Nature Cl_2 was supplied by Matheson with a stated purity of better than 99.9%, which was used in this experiment as delivered. The gas pressure was measured by a MKS Baratron capacitance manometer. The light source intensity, the gas pressure, and the fluorescence intensities were simultaneously monitored and analyzed by an IBM microcomputer.

III.   RESULTS AND DISCUSSION

A.   Photoabsorption Cross Section

The photoabsorption cross section of Cl_2 in the 105-145 nm region is shown in Fig. 1 for a monochromator resolution set at 0.1 nm. The cross section was derived from the light attenuation under the condition that the absorbance increases linearly with increasing Cl_2 pressure. The pressure range used in the absorption measurement depends on the absorption cross section, that is, the higher the absorption cross section, the smaller is the pressure range.

As shown in Fig. 1, the absorption spectrum is dominated by

4

sharp discrete structures. Thus, the measured cross section depends on the monochromator resolution. The apparent absorption cross section given in Fig. 1 represents the average value over the 0.1 nm bandwidth. The uncertainty is estimated to be $\pm$ 10% of the given value. The wavelengths given by the high resolution spectra of Douglas[3] and Moeller et al.[4] were used as the wavelength reference in this experiment.

In contrast to the absorption cross section, the oscillator strength does not depend on the resolution. The oscillator strength can be determined[9] from the measured average absorption cross section by

$$f = 11.3 \quad \int \sigma(\lambda)\, d\lambda / \lambda^2$$

where $\sigma(\lambda)$ is the absorption cross section in unit of Mb $(10^{-18}\ cm^2)$ and λ is the wavelength in unit of nm. The oscillator strengths for the strong absorption bands are listed in Table I. The experimental uncertainty is estimated to be $\pm$10% of the given value.

The oscillator strengths for the $2^1\Pi_u$ and $2^3\Pi_u \leftarrow X^1\Sigma_g^+$ transitons have been recently calculated by Grein et al.[7] whose values are 0.0699 and 0.0084, respectively. The sum of the measured oscillator strengths for the $2^1\Pi_u$ ($=0-3$) $\leftarrow X^1\Sigma_g^+$ is 0.0635 as shown in Table I and Fig. 1. This measured value agrees very well with the calculated one. The oscillator strength for the $2^3\Pi_u$ ($v'=0-3$) $\leftarrow X^1\Sigma_g^+$ transition determined from the data shown in Fig. 1 is 0.017. This value is larger than the calculated value by a factor of 2. However, depending on the energy difference between the $2^3\Pi_u$ and $2^1\Pi_u$ states the calculated value[7] could be adjusted to 0.0122. This higher value agrees

reasonably well with our measurement. In considering both the experimental and theoretical uncertainties, the agreement is quite good.

The absorption bands are classified into Rydberg series, as shown in Fig. 1. The wavelengths, the wavenumbers, and the peak absorption cross sections for these Rydberg states are listed in Tables II-IV. The justification of the Rydberg state assignment is discussed below.

B. Rydberg States

The electronic configurations of Cl_2 have been studied by Lee and Walsh[1], for which the ground state, $X^1\Sigma_g^+$, is given by

$$---(\sigma_g 3p)^2(\pi_u 3p)^4(\pi_g 3p)^4$$

The potential curves of Cl_2 have been calculated by Peyerimhoff and Buenker[5]. The singlet states relevant to the interpretation of the observed strong transitions are shown in Fig. 2. Although the vertical excitation energies may need to be adjusted[7], these potential curves are still good to serve the purpose of present discussion. The potential curves for most excited states are complicated by the perturbation of the ionic states such that they result in double wells.

The $1^1\Sigma_u^+$ ($\pi_g \rightarrow 4p\pi$) state is an ionic state which fluoresces. The vibrational levels of this ionic state were studied in great detail by Moeller et al.[4], and the rotational spectra were analyzed by Douglas[3]. The fluorescence quantum yield for this state is close to 1 (see Discussion in the next section).

The $2^1\Pi_u$ state results from the $\pi_g \rightarrow 4p\sigma$ Rydberg transition.[5] The effective quantum number of this Rydberg state

6

is $n^* = 2.46$ (a quantum defect of $\delta = 1.54$ for n=4), where the ionization potential[10] of 92,590 cm^{-1} (11.48 eV) was used for the calculation of n^*. Using this quantum defect, the Rydberg states with n = 5 and 6 are found as listed in Table II and also indicated in Fig. 1. The spin-orbital splitting for the first Cl_2^+ state, $X^2\Pi_{g1/2,3/2}$, is same as its vibrational frequency, thus, the photoelectron spectrum shows a single vibrational progression.[11,12] The characteristics of the Rydberg states are usually the same as its converging ion state, that is the spin-orbital splitting for the $2^1\Pi_u$ and $^3\Pi_u$ states are also similar to the vibrational frequency as shown in Fig. 1.

The vibrational levels of the $2^1\Sigma^+$ state were assigned by Moeller et al.[4] The vibrational levels are now extended to v'=15 using the fluorescence excitation spectrum observed in the current experiment (see discussion in the next section). The $2^1\Sigma_u^+$ state results from the $\pi g \to 4p\pi$ Rydberg transition[5] (which may mix with the $\sigma g \to \sigma_u$ transition) with an effective quantum number of $n^* = 2.75$ (a quantum defect of $\delta = 1.25$ for n=4). Using this quantum defect, the n = 5 and 6 Rydberg states are found as listed in Table III and also indicated in Fig. 1.

The absorption spectrum in the 105-115 nm region is complicated, and the transitions were not assigned before. According to the potential curves shown in Fig. 2, the absorption in this wavelength region likely corresponds to the $3^1\Pi_u \to X^1\Sigma_g^+$ transiton. The calculated vertical excitation energy for this transition[7] is 90501 cm^{-1} (110.50 nm). The $3^1\Pi_u$ state results

from the $\sigma_u \rightarrow 4s$ Rydberg transiton[5], which converges to the second Cl_2^+ state, $A^2\Pi_i$. The vibrational levels of this ion state were observed to be a chaotic distribution.[13] The vibrational levels were classified into five vibrational progressions, that is, system I (a), (b) and (c) and system II (d) and (e). Since the $3^1\Pi_u$ state is the Rydberg state converging to the $Cl_2^+(A)$ state, the vibrational spacings of these two states should be similar. This expectation is indeed true. The absorption structures in the 105-115 nm region are arranged into system I (a), (b) and (c) and system II (d) and (e) as shown in Fig. 1 in corresponding to the vibrational progressions of the Cl_2^+ (A) state. The wavelengths, vibrational frequencies, spacings, and peak corss sections for system I (a) and (b) are listed in Table IV. Both the chaotic distributions observed in the Rydberg and ion states indicate that the chaotic vibrational distribution occurs in nature. The other possibility[13] that the chaotic vibrational distribution of the ion state is due to perturbation seems unlikely. The oscillator strengths for the system I (c) and system II (d) and (e) are relatively weak when compared with system I (a) and (b). The weaker systems may be due to the triplet state, $3^3\Pi_u$, similar to the case of $2^3\Pi_u$ mixed with $2^1\Pi_u$.

Taking the ionization potential[11,12,14] of the $Cl_2^+(A)$ state at onset as 13.96 eV, the effective quantum number for the first vibrational level of system I(a) is $n^* = 2.10$ (the quantum defect $\delta = 1.90$ for n=4). Considering the quantum defect of $\delta = 1.54$ for the p-electron, this quantum defect of $\delta = 1.90$ for the s-electron is reasonable. This further supports the assignment of

8

the $3^1\Pi_u$ Rydberg state.

C. Fluorescence Cross Sections

The cross sections for the production of UV and VUV fluorescence measured at a monochromator resolution of 0.2 nm are shown in Fig. 3. The absorption cross section measured at the same resolution is also shown in Fig. 3 for comparison. The peak absorption cross section in Fig. 3(a) is generally smaller than that in Fig. 1, because the monochromator resolution used for Fig. 3(a) is lower.

The VUV fluorescence was detected by a solar blind PMT whose response was in the 115-180 nm region, and the UV fluorescence by a PMT (EMI 9558QB) in the 180-300 region (see the Experimental Section for the absolute calibration). The uncertainty for the UV fluorescence cross section is estimated to be $\pm$ 30% of the given value, but for the VUV fluorescence the uncertainty can be a factor of 2.

The fluorescence from the $1^1\Sigma_u^+$ ionic state has been observed by several investigators,[4,15,16] although the absolute fluorescence cross section was not reported before. The fluorescence excitation spectrum in the 130-140 nm region has been studied by Moeller et al.[4] They also dispersed the fluorescence spectrum which covers from the excitation wavelength to 208 nm[4]. In our experiment, when an optical filter (transmitting wavelengths longer than 300 nm) was placed in front of PMT, the fluorescence disappeared. This confirms that the fluorescence spectrum is limited in the UV and VUV regions. The VUV fluorescence likely results from the $1^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition,

and the UV fluroescence from the $1^1\Sigma_u^+ \rightarrow 1^1\Pi_g$ transition.

The VUV and UV fluorescence excitation spectra for the $1^1\Sigma_u^+$ state are generally the same as the absorption spectrum as shown in Fig. 3, except for the band at 136.2 nm where the VUV fluorescence is relatively more intense than the UV fluorescence. The cross section for the VUV fluorescence is larger than the UV fluorescence by a factor of about 5. At each wavelength in the 135-150 nm region, the sum of the VUV and UV fluorescence cross sections is about equal to the absorption cross section, indicating that the fluorescence quantum yield is nearly equal to 1. This result shows that the $1^1\Sigma_u^+$ state is not predissociative.

At low gas pressure, both the UV and VUV fluorescence intensities of the $1^1\Sigma_u^+$ state increase with increasing gas pressure as shown in Fig. 4(a), where the excitation wavelength is 135.2 nm. The fluorescence intensity does not increase further at high gas pressure. This saturation effect is due to the pre-absorption of light source intensity by the gas between the entrance and the PMT view region. The absorbance, which is defined as $\ln(I_0/I)$ for the light source intensities with (I) and without (I_0) Cl_2 in the gas cell, is also shown in Fig. 4(a) for comparison. The saturation of the absorbance at high gas pressure is due to total absorption of some rotational lines by the gas. For the absorption cross section measurement the pressure is limited to the region that the absorbance is linearly dependent on the gas pressure as mentioned before.

The fluorescence from the second ionic state, $2^1\Sigma_u^+$, is not well studied. We observe that this state fluoresces up to v'=15 as shown in Fig. 3(b). The wavelengths of the observed

10

vibrational levels are listed in Table II. This result demonstrates that the fluorescence excitation spectrum provides useful information to identify electronic states, which are otherwise difficult to be identified from the absorption spectrum because of overlapping of several electronic transitions. The fluorescence quantum yield for the $2^1\Sigma_u^+$ state is generally less than 1, indicating that this state is partially dissociative. This state may be heavily perturbed by the triplet states that do not fluoresce.

At wavelengths shorter than 109.7 nm, a VUV fluorescence band appears as shown in Fig. 3(b). At low gas pressure, the VUV fluorescence intensity increases linearly with gas pressure as shown in Fig. 4(b). At high gas pressure, the VUV fluorescence intensity is saturated due to pre-absorption. The VUV fluorescence is saturated at the gas pressure lower than that for the absorbance. This is caused by the fact that the VUV fluorescence is absorbed by the Cl_2 gas before it reaches the window of the solar blind PMT. Because of such difficulty as well as the spectral response being not corrected, the uncertainty for the absolute VUV fluorescence cross section in this excitation wavelength region is qutie high (a factor of 2-3). Nevertheless, the fluorescence quantum yield for this excitation band is quite large. The excitation energy of this absorption band is higher than the ionization potential, thus, it is a so-called "superexcited state". The fluorescence yield for a "superexcited state" is usually small. The high fluorescence yield observed in this excitation band presents an interesting

case.

When the Cl_2 pressure increases, fluorescence in the UV region appears. The UV fluorescence intensity depends on the gas pressure quadratically as shown in Fig. 4(b), where the excitation wavelength is 108.25 nm. This result indicates that the UV fluorescence is not primarly produced by photoexcitation but by collisional-induced excitation. The UV fluorescence may result from energy transfer from excited species to Cl_2, where the excited species are produced by photoexcitation. The cross section for the production of UV fluorescence by primary photoexcitation process is practically zero. The dashed curve shown in Fig. 3(c) is only an excitation spectrum, which does not represent the absolute fluorescence cross section for the primary photoexcitation process. It is noted that the UV fluorescence has a significant intensity at few mtorr. This indicates that the excited state has a sufficient long lifetime which could be longer than 20 μs as estimated from gas collision kinetics. This lifetime is much longer than the lifetime of the VUV radiative state that is expected to be in the ns region. This result indicates that the UV and VUV fluorescence are produced from different states.

The nature of the fluorescence band in the 106-110 nm region is not clear and it deserves to be studied more. The excitation spectra for both UV and VUV fluorescence at pressures 2.0, 4.9 and 11.1 mtorr are shown in Fig. 5. The intensity for the VUV fluorescence increases linearly with Cl_2, but the UV fluorescence increases quadratically for the entire excitation band. The light source intensity in this wavelength region is nearly

12

constant, and it is not corrected in Fig. 5. It is noted that the excitation spectrum for the UV fluorescence is different from the VUV fluorescence, indicating that they are produced from different excited states as expected from the estimation of the different lifetimes. Similar structures appear at both the UV and VUV excitation spectra as well as repeatly shown in the absorption spectrum.

The VUV fluorescence is not produced from the excited atomic chlorine, because the excitation photon energy is not enough to produce excited chlorine atoms. For instance, the dissociation energy[17] of Cl_2 is 2.479 eV, the wavelength threshold for producing the $Cl(^2P-^2P_{3/2})$ emission of 134.7 nm is 106.1 nm. This threshold wavelength is shorter than the threshold of the fluorescence band that starts at 110 nm.

IV. CONCLUDING REMARKS

The photoabsorption and fluorescence cross sections of Cl_2 in the VUV region are measured using synchrotron radiation as a light source. The structures shown in the absorption spectrum are classifed into Rydberg series. The structures shown in the photoabsorption spectrum are generally observed in the threshold-electron-impact excitation spectrum[18] and the electron energy loss spectrum.[19] The resolution for the current photoabsorption spectrum is much higher than the electron spectra,[18,19] thus, the structures are much better resolved and assigned.

The Fluorescence yield for the $1^1\Sigma_u^+$ state is very high (close to 1). Thus, this fluorescence system can be used to

develop techniques for a remote sensing of Cl_2 in various environments, such as plasma etching vessel. In other case, the fluorescence cross section of Cl_2 at 147 nm is so small that the existence of Cl_2 in the flow tube does not affect the HO_2 kinetics measurement. The fluorescence excitation spectrum is also a useful tool for spectroscopic study. As an example, the vibrational levels of the $2^1\Sigma_u^+$ ionic state are observed up to v'=15 with the aid of fluorescence excitation spectrum. It is interesting that the absorption band in the 106-110 nm region has a large quantum yield to produce VUV fluorescence, but the yield for the UV fluorescence is essentially zero. The UV fluorescence is produced by a collisonal excitation process. The nature of this excitation process is not understood and it will be interesting to pursue further.

ACKNOWLEDGEMENT

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Table I

Integration of absorption cross section over wavelength, $\int \sigma d\lambda$, in units of Mb·nm and oscillator strength, f, in units of 10^{-3} for the major absorption bands.

wavelength (nm)	$\int \sigma(\lambda)d\lambda$ (Mb·nm)	f(10^{-3})
111.50-111.77	21.7	19.7
112.58-112.85	22.9	20.4
113.17-113.39	19.0	16.7
113.66-114.01	29.4	25.6
114.12-114.47	22.4	19.4
116.96-117.15	10.1	8.3
117.82-117.98	9.7	7.9
124.74-125.00	9.1	6.6
126.36-126.63	12.7	9.0
127.84-128.38	31.6	21.8
130.84-131.14	5.9	3.9
132.00-132.19	19.6	12.7
133.11-133.30	36.2	23.1
134.22-134.47	37.8	23.7
135.01-135.95	83.5	51.5
135.95-136.49	43.0	26.2

Table II

Effective quantum number, n^*, wavelength, λ(nm), wavenumber, ν(cm^{-1}), vibrational spacing, $\Delta\nu$(cm^{-1}), and peak absorption cross section, σ_p(Mb), for the $\tilde{\pi}_g \to np\sigma$ Rydberg Series.

n	n^*	v'	λ(nm)	ν(cm^{-1})	$\Delta\nu$(cm^{-1})	σ_p(Mb)
4	2.46	0	134.33	74,443		301.5
$(2^1\Pi_u)$		1	133.22	75,064	621	315.6
		2	132.10	75,700	636	157.6
		3	131.04	76,313	613	39.0
		4	130.14	76,840	527	
		5	129.22	77,387	547	
5	3.46	0	119.87	83,424		35.3
		1	119.02	84,019	595	42.9
		2	118.18	84,617	598	
6	4.41	0	115.02	86,941		
		1	114.40	87,413	472	
∞			108.00	92,590		

Table III

Spectroscopic data for the $\pi g \rightarrow np\pi$ Rydberg Series

n	n*	v'	λ(nm)	ν(cm^{-1})	Δν(cm^{-1})	σ$_p$(Mb)
4	2.75	0	128.01	78,119		133.9
($2^1 \Sigma_u^+$)		1	126.45	79,083	964	84.3
		2	124.89	80,070	987	58.6
		3	123.66	80,867	797	28.2
		4	122.33	81,746	879	
		5	121.17	82,529	783	
		6[a]	120.18	83,209	680	
		7	118.94	84,076	867	
		8	117.92	84,803	727	
		9	116.81	85,609	806	
		10	116.02	86,192	583	
		11	115.18	86,821	629	
		12	114.28	87,504	683	
		13	113.37	88,207	703	
		14	112.59	88,818	611	
		15	111.81	89,437	619	
5	3.75	0	117.92	84,803		84.9
		1	117.08	85,412	609	94.9
		2	116.32	85,970	558	54.7
		3	115.50	86,580	610	
6	4.68	0	114.18	87,581		
∞			108.00	92,590		

a   The wavelengths for the vibrational levels from v'=6 to 15 were determined from
the fluorescence excitation spectra.

Table IV

Spectroscopic data for the $\pi_u \rightarrow 4s\ (3^1\Pi_u)$ Rydberg Transition

Vibrational Series		λ(nm)	ν(cm^{-1})	$\Delta\nu$(cm^{-1})	σ_p (Mb)
I	a	113.91	87,789		143.1
		112.75	88,692	903	130.3
		111.65	89,566	874	101.5
		110.72	90,318	752	
		109.70	91,158	840	
		108.94	91,794	636	
		108.20	92,421	627	
		107.46	93,058	637	
		106.72	93,703	645	
	b	113.28	88,277		122.6
		112.06	89,238	961	
		110.98	90,106	868	
		110.02	90,893	787	
		109.25	91,533	640	
		108.49	92,174	641	
		107.75	92,807	633	
		107.03	93,432	625	

FIGURE CAPTIONS

Fig. 1   Photoabsorption cross section of Cl_2 in the 105-145 nm
         region measured with 0.1 nm resolution.   The wavelength
         positions for the Rydberg transitions are indicated.

Fig. 2   The potential curves of the singlet states relevant to
         the discussion in this paper.   These curves are adopted
         from Ref. 5.

Fig. 3   (a) absorption,   (b) VUV fluorescence, and (c) UV
         fluorescence cross sections measured with 0.2 nm
         resolution.   The vibrational levels of the $2^1\Sigma_u^+$ are
         indicated in (b).   The dashed curve in (c) is an
         excitation spectrum which does not represent absolute
         value.

Fig. 4   The pressure dependence of the absorbance, VUV and UV
         fluorescence intensities measured at (a) 135.20 nm and
         (b) 108.25 nm.

Fig. 5   Dependence of excitation spectra of (a) VUV and (b) UV
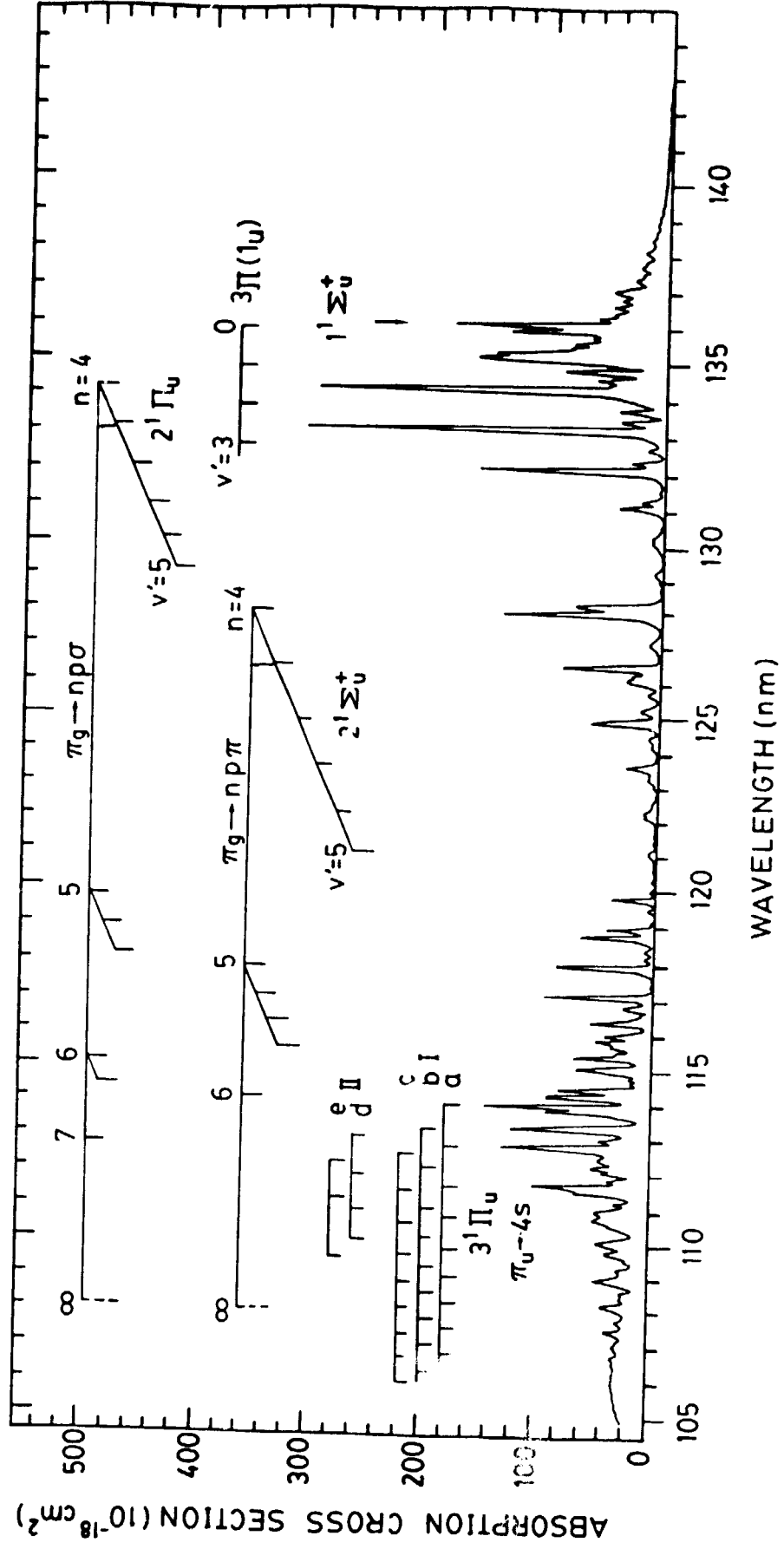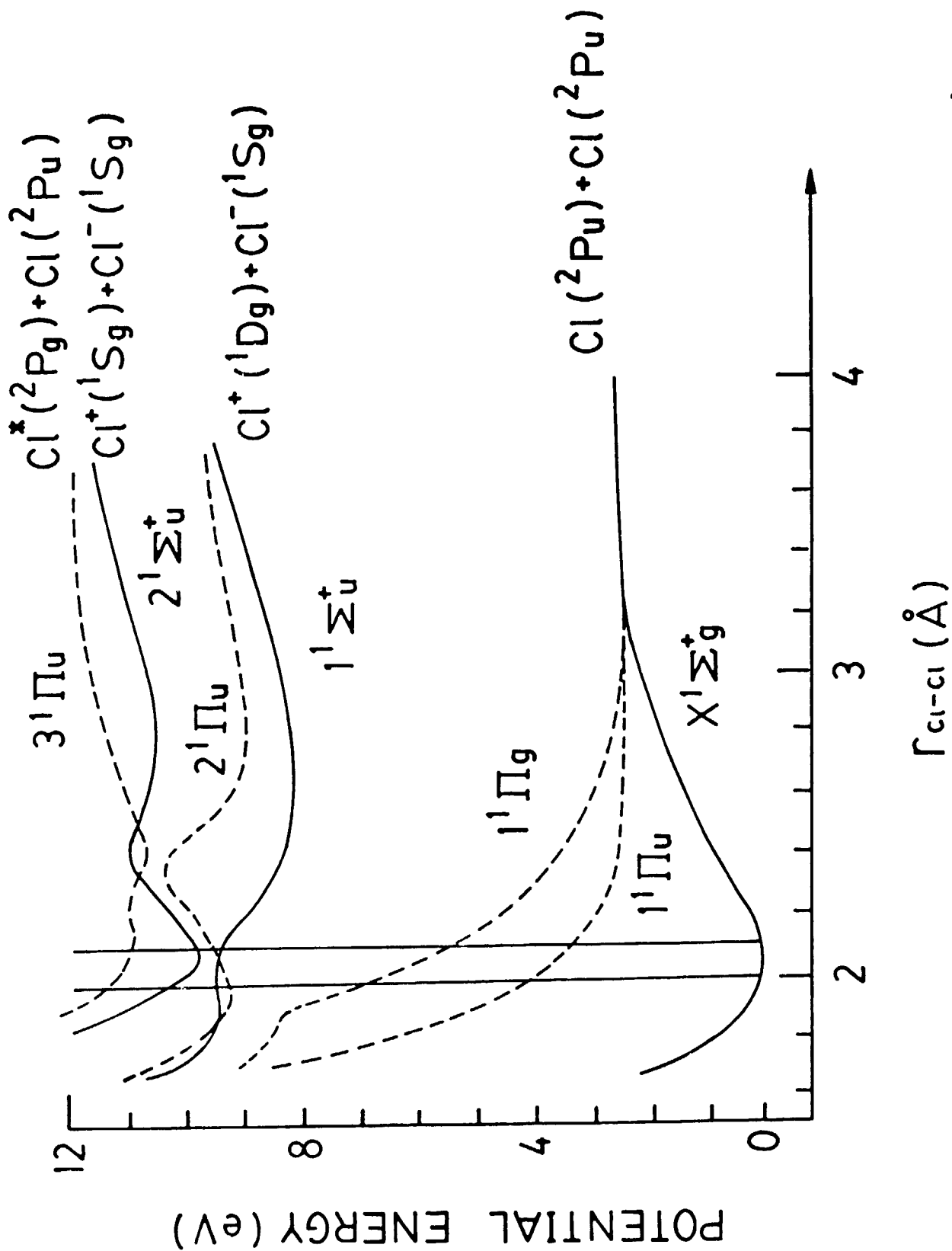   fluorescence on Cl_2 pressures of (1) 2.0, (2) 4.9, and
         (3) 11.1 mtorr.
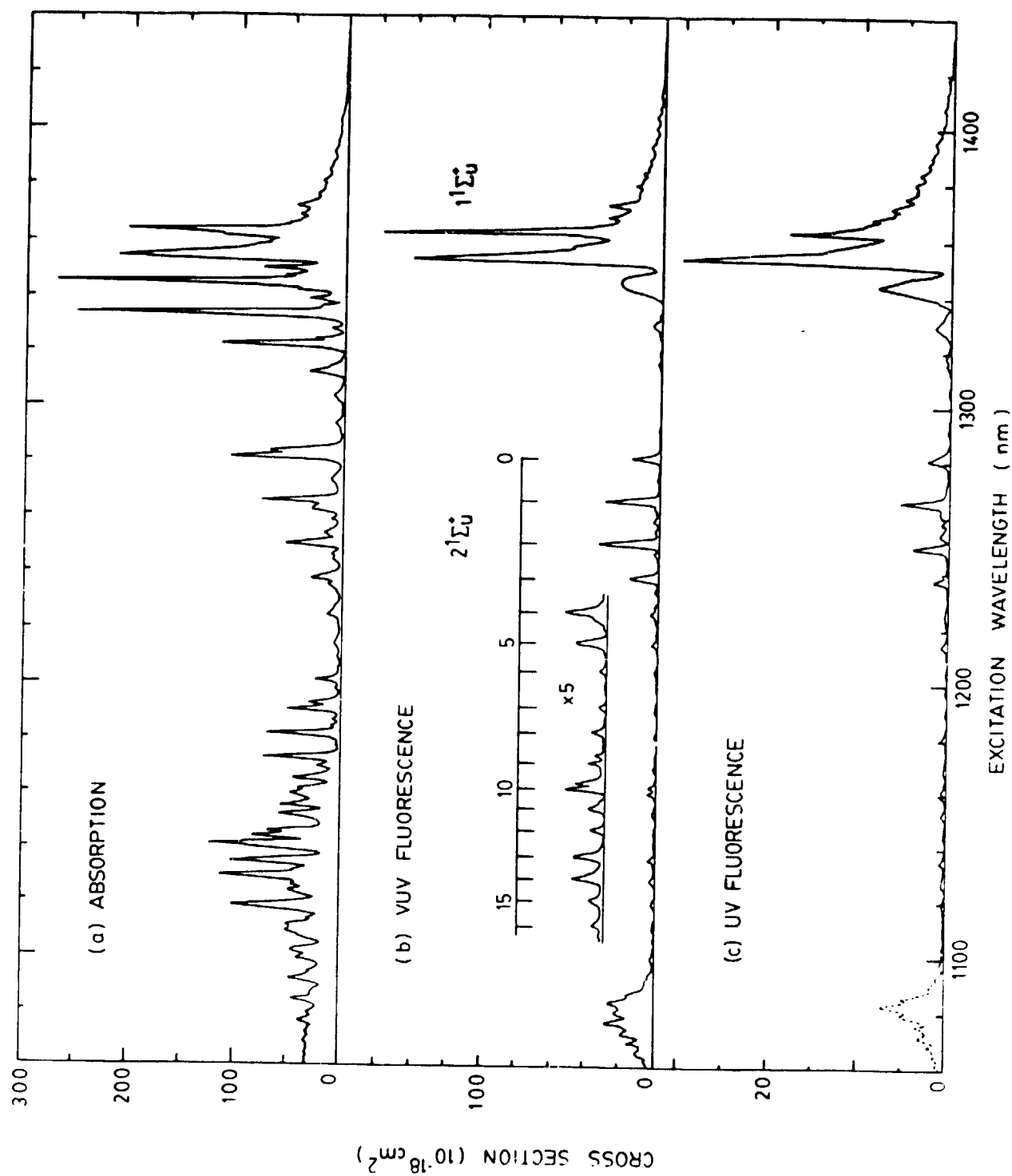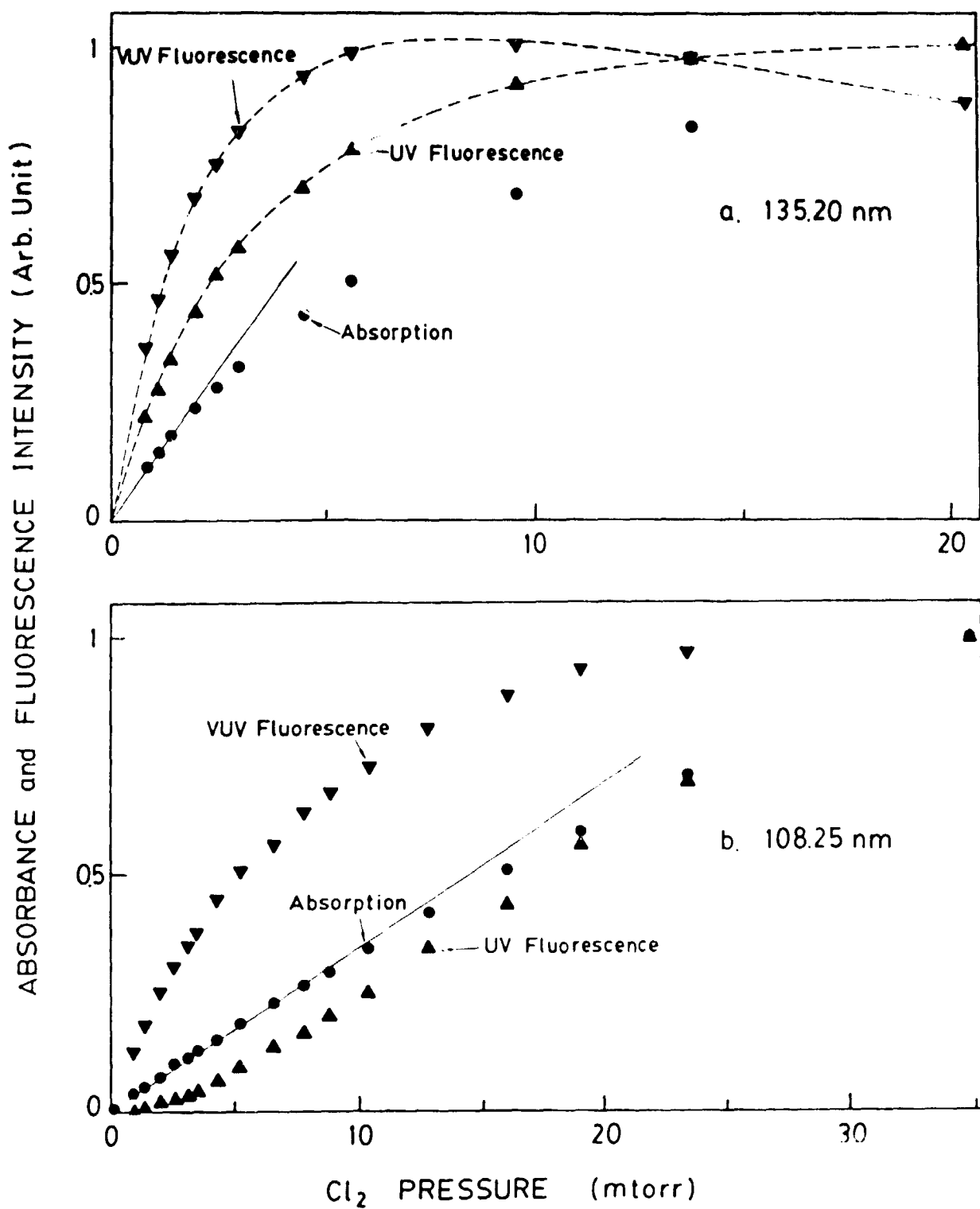
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5