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CF₂ and CFC1 Fluorescence from VUV
Excitation of C₂F₃Cl

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ABSTRACT

The photoexcitation process of C₂F₃Cl molecule was investigated in the 106-230 nm region using synchrotron radiation as a light source. Photoabsorption and fluorescence cross sections were measured and used to determine the fluorescence quantum yield. Fluorescence yield starts to appear at 170 nm and increases to about 2% at 155 nm. The fluorescence spectra were dispersed to identify the emitting species. At the excitation wavelength of 155 nm, the emission system is CFC1 ($\tilde{A}-\tilde{X}$), and at 123.9 nm, both the CF₂($\tilde{A}-\tilde{X}$) and CFC1 ($\tilde{A}-\tilde{X}$) systems are observed. The dissociation processes that produced these excited species are discussed.

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I. INTRODUCTION

In a recent study of reaction kinetics of $\text{HO}_2 + \text{O}_3$ by detecting HO_2 with photofragment emission in our laboratory, emission from excitation of $\text{C}_2\text{F}_3\text{Cl}$ at 147 nm was observed when it was introduced into the system as a scavenger for the OH radical [1]. This motivated us to investigate the photochemistry of $\text{C}_2\text{F}_3\text{Cl}$ in vacuum ultraviolet (VUV) region in order to understand the nature of the UV emission. The VUV absorption spectrum of $\text{C}_2\text{F}_3\text{Cl}$ is itself of interest in understanding the Rydberg states of chlorofluoroethylenes, which show an absorption character similar to that of ethylene. The photoexcitation process of $\text{C}_2\text{F}_3\text{Cl}$ is also interesting for the possible role it plays in atmospheric chemistry, because it is a member of halocarbons and releases F and Cl atoms into the atmosphere by solar radiation.

Photoexcitation of $\text{C}_2\text{F}_3\text{Cl}$ may produce excited dihalogen carbene radicals of CF_2 and CFC1 which are known to have strong transitions in the ultraviolet (UV) region. These radicals can be generated from $\text{F}_2\text{C}=\text{CFC1}$ by chemical reaction with oxygen atoms [2,3], UV photolysis [4-6], and infrared multiphoton dissociation [7]. The UV emission system of $\text{CF}_2(\tilde{\text{A}}^1\text{B}_1 - \tilde{\text{X}}^1\text{A}_1)$ has been extensively investigated [8,9]; but, the $\text{CFC1}(\tilde{\text{A}}^1\text{A}'' - \tilde{\text{X}}^1\text{A}')$ system has been studied only recently [7,10]. Up-to-date information regarding the photoabsorption process of $\text{C}_2\text{F}_3\text{Cl}$ has been summarized in a recent book by Robin [11].

II. EXPERIMENTAL

The synchrotron radiation experiment was carried out in the electron storage ring at the University of Wisconsin. Experimental details have been described in a previous publication [12]. Synchrotron radiation was dispersed by a 1-m vacuum monochromator before entering a gas cell. UV fluorescence was detected in the direction perpendicular to the light beam by an EMI (9558QB) photomultiplier tube (PMT). Light source intensity was measured by another PMT attached to the end of the gas cell. The VUV light source was converted to UV light by sodium salicylate coated outside a LiF window. The optical path length for absorption measurement was 39.1 cm. C_2F_3Cl was supplied by Matheson with a purity better than 99.0%; no further purification was made.

The apparatus for dispersing the fluorescence spectrum has been described previously [13]. A pulsed discharge lamp associated with a 1-m vacuum monochromator (McPherson 225) was used as the light source. Fluorescence was dispersed by a 0.3-m monochromator (McPherson 218) and detected by a PMT (EMI 9558QB). Atomic emission lines of CIV at 155 nm and NV at 123.9 nm were used to excite C_2F_3Cl . A gated photon counting system was used to process the fluorescence signal.

III. RESULTS

The photoabsorption cross section of C_2F_3Cl at 106-225 nm was measured. The absorbance $\ln(I_0/I)$ was linearly dependent on C_2F_3Cl pressure up to 100 mtorr at 105-180 nm. In the 180-230 nm

region, C_2F_3Cl gas up to 10 torr was used because of weak absorption. The absorption spectrum obtained at a resolution of 0.2 nm is shown in Figure 1, curve a. Experimental uncertainty for the absorption cross section is estimated to be within 10% of the given value. Positions of the V - N transition [14] and the Rydberg series assigned by Scott and Russel [15] are also indicated in Figure 1.

The total fluorescence cross section measured simultaneously with the absorption cross section is shown in Figure 1, curve b. The fluorescence cross section was calibrated against the fluorescence of OH(A-X) from VUV photodissociation of H_2O for which fluorescence cross section has been measured [12]. The PMT response was nearly constant in the 185-400 nm region and decreased at the longer wavelength. Since the fluorescence is essentially in the UV region, the PMT response was not corrected in the fluorescence cross section measurement.

The fluorescence quantum yield was determined as a ratio of the fluorescence cross section to the absorption cross section. The fluorescence quantum yield in the 106-170 nm region is shown in Figure 2. Experimental uncertainty for the fluorescence cross section is estimated to be within 30% of the given value.

Fluorescence spectra from the photodissociation of C_2F_3Cl by atomic lines from a discharge lamp are shown in Figures 3 and 4. Figure 3a shows the dispersed emission spectrum excited at 155 nm; Figure 3b shows the spectrum when 1 atm of Ar was added for the vibrational relaxation of excited species. When the

vibrational energy was relaxed, the emission shifted to red. This spectrum is identified as the $\text{CFC1}(\tilde{\text{A}}-\tilde{\text{X}})$ system by comparing it with the laser-induced-fluorescence spectrum [7]. The radiative lifetime of $\text{CFC1}(\tilde{\text{A}}-\tilde{\text{X}})$ is 700 ± 10 ns [7]. Thus, at low gas pressure, the quenching of the emission by parent molecule is negligible.

The emission spectrum produced by photoexcitation of $\text{C}_2\text{F}_3\text{Cl}$ at 123.9 nm is shown in Figure 4. The long wavelength section of this spectrum is similar to Figure 3a, but at wavelengths shorter than 350nm, the emission is mainly due to the $\text{CF}_2(\tilde{\text{A}}-\tilde{\text{X}})$ system [8,9]. These emitting species may not be simultaneously produced by a single photodissociation process such as, $\text{C}_2\text{F}_3\text{Cl} \rightarrow \text{CF}_2^* + \text{CFC1}^*$, because this requires energy higher than 10 eV. The photodissociative excitation of $\text{C}_2\text{F}_3\text{Cl}$ will be discussed later.

IV. DISCUSSION

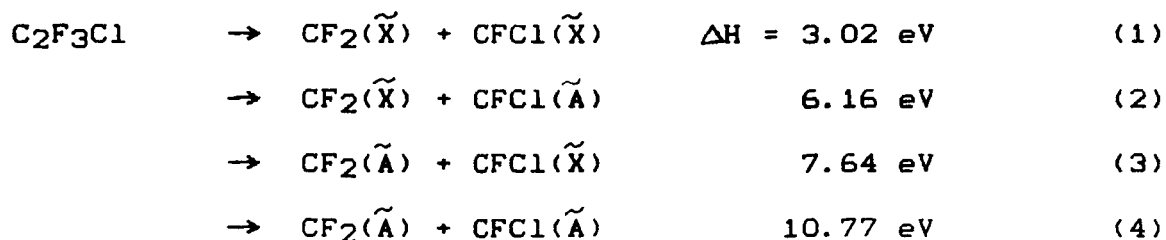
A. Photoabsorption Spectrum

$\text{C}_2\text{F}_3\text{Cl}$, like other chlorofluoroethylenes, has an absorption spectrum quite similar to that of ethylene [11]. The electronic transition of an electron excited from the π orbital of the C=C bond (the ground state, N) to the π^* orbital forms a triplet state, T, and a singlet state, V. The electron may also be excited to Rydberg states, R. The absorption spectra of ethylene-type molecules have been extensively investigated in the VUV region. The VUV excitation process is primarily due to the V and $R \leftarrow N$ transitions; however, the vibronic structures for these molecules have not yet been thoroughly studied [11].

Scott and Russel [15] have assigned two Rydberg states for C_2F_3Cl among other chlorofluoroethylenes. The Rydberg series converging to the first ionization limit are shown in Figure 1. Using photoelectron spectroscopy, Lake and Thompson [16] determined the vertical ionization potential (transition of maximum probability) of C_2F_3Cl to be 10.24 eV (121.1 nm), and adiabatic ionization potential (transition to $v'=0$ of the upper state) to be 9.84 eV (126 nm). The excited states of C_2F_3Cl have been compared with those of other halogenated-ethylenes by electron-impact spectroscopy [17, 18]. The broad continuum extending from about 140 nm to 225 nm is assigned to the V - N transition overlapped with Rydberg states [15]. This continuum is superimposed with the vibrational structure of the C=C stretching mode.

B. Fluorescences of CF_2 and $CFC1$.

Energy thresholds for the photodissociative excitation process of C_2F_3Cl can be determined from the following heats of formation: $\Delta H_f^0 = -120.8 \pm 1.1$ kcal/mol for C_2F_3Cl [19], -49 ± 3 kcal/mol for CF_2 [20], and -2 ± 7 kcal/mol for $CFC1$ [20]. The electronic energies for $CF_2(\tilde{A}^1B_1)$ and $CFC1(\tilde{A}^1A'')$ are 4.616 [8] and 3.135 eV [7], respectively. The energies required for various processes are as follows:



The other radicals such as C_2F_3 or C_2F_2Cl may not emit strongly, because the fluorescence spectra shown in Figures 3 and 4 are mainly from CF_2 and $CFC1$.

The spectrum of quantum yield shows two broad peaks around 123 nm and 155 nm. Since the excitation of C_2F_3Cl at 155 nm produces $CFC1(\tilde{A})$ only, the quantum yield in the 135-170 nm region is presumably due to $CFC1(\tilde{A})$ only, while the second peak at 123 nm probably indicates the existence of a state producing $CF_2(\tilde{A})$. As shown in Figure 2, the threshold wavelength for the production of $CFC1(\tilde{A})$ is at 170 nm (7.29 eV), and it is likely around 135 nm (9.18 eV) for $CF_2(\tilde{A})$. These fluorescence thresholds are much higher than the thermochemical thresholds of processes (2) and (3). Thus, the vertical energies of the dissociative states that produce $CF_2(\tilde{A})$ and $CFC1(\tilde{A})$ are higher than the dissociation thresholds.

The fluorescence quantum yield is determined from the transition probability for excitation to a repulsive state (direct dissociation) or the interaction strength between a discrete state and a dissociative state (predissociation). Since the fluorescence quantum yields for both the vibrational bands and the absorption continuum in the 140-170 nm region are about the same, the strength for producing the $CFC1(A)$ by either direct photodissociation process or predissociation process is about the same. The peak for the spectrum of fluorescence yield can be used to determine the vertical energy of the dissociative state which is about 8.0 eV for $CFC1(\tilde{A})$ and about 10 eV for $CF_2(\tilde{A})$.

For the 10 eV band, the peak wavelength of quantum yield may be affected by the onset of ionization process. In general, the fluorescence quantum yield decreases at wavelengths shorter than ionization limit.

The shift of the CFC1 emission spectrum to red when Ar is added as shown in Figures 3a and 3b indicates that $\text{CFC1}(\tilde{\text{A}})$ is vibrationally excited. Based on the threshold energy of process (2), an excess energy of 1.84 eV is available. This excess energy is enough to excite the molecule into high vibrational quantum numbers which can be calculated from the spectroscopic data (6,9). However, the vibrational spectrum shown in Figure 3 is very complicated, it is difficult to assign vibrational levels.

V. CONCLUSION

The photoabsorption and fluorescence cross sections of $\text{C}_2\text{F}_3\text{Cl}$ have been measured in the 106-230 nm region. Fluorescence spectra have been dispersed and identified to be the $\text{CF}_2(\tilde{\text{A}}^1\text{B}_1 - \tilde{\text{X}}^1\text{A}_1)$ and $\text{CFC1}(\tilde{\text{A}}^1\text{A}'' - \tilde{\text{X}}^1\text{A}')$ systems. The spectrum of fluorescence quantum yield shows two dissociative states. The threshold wavelengths for producing $\text{CFC1}(\tilde{\text{A}})$ and $\text{CF}_2(\tilde{\text{A}})$ were determined to be 170 and 135 nm, respectively.

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FIGURE CAPTIONS

- Fig. 1. Photoabsorption and fluorescence cross sections of C_2F_3Cl in the 106-230 nm region in units of $Mb(10^{-18} \text{ cm}^2)$. The wavelength positions of the $V \leftarrow N$ transition and the Rydberg series assigned by Scott and Russel are indicated.
- Fig. 2. Fluorescence quantum yield in the 106-175 nm region. The dashed line represents an average value.
- Fig. 3. Fluorescence spectra produced by photoexcitation of C_2F_3Cl at 155 nm. (a) Pure C_2F_3Cl of 80 mtorr and (b) 1 atmosphere Ar was added to (a). The monochromator resolution was 4 nm. The fluorescence spectrum is identified to be the $CFCl(\tilde{A}-\tilde{X})$ system.
- Fig. 4. Fluorescence spectrum produced by photoexcitation of 80 mtorr C_2F_3Cl at 123.9 nm. The monochromator resolution was 4 nm.

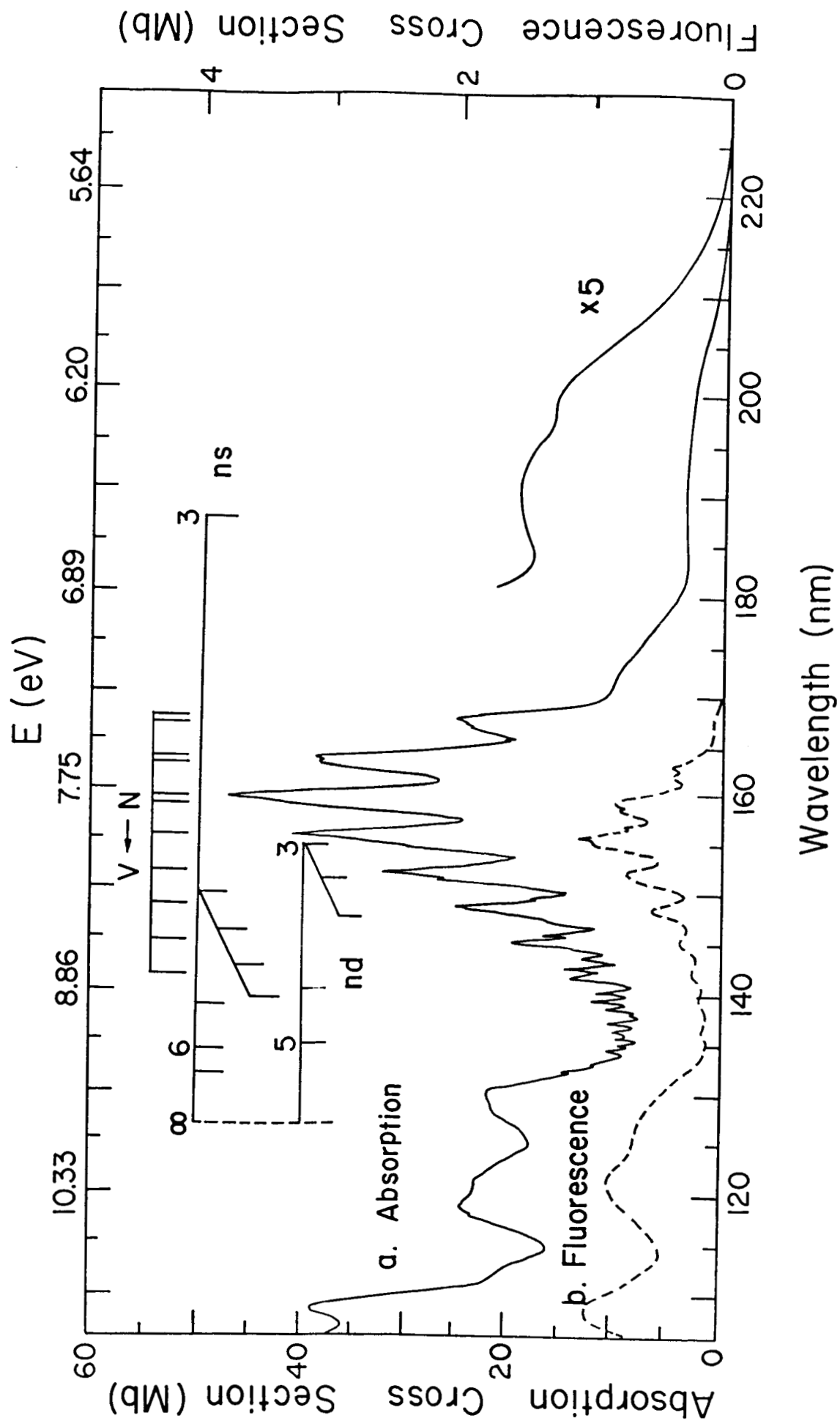


Fig. 1

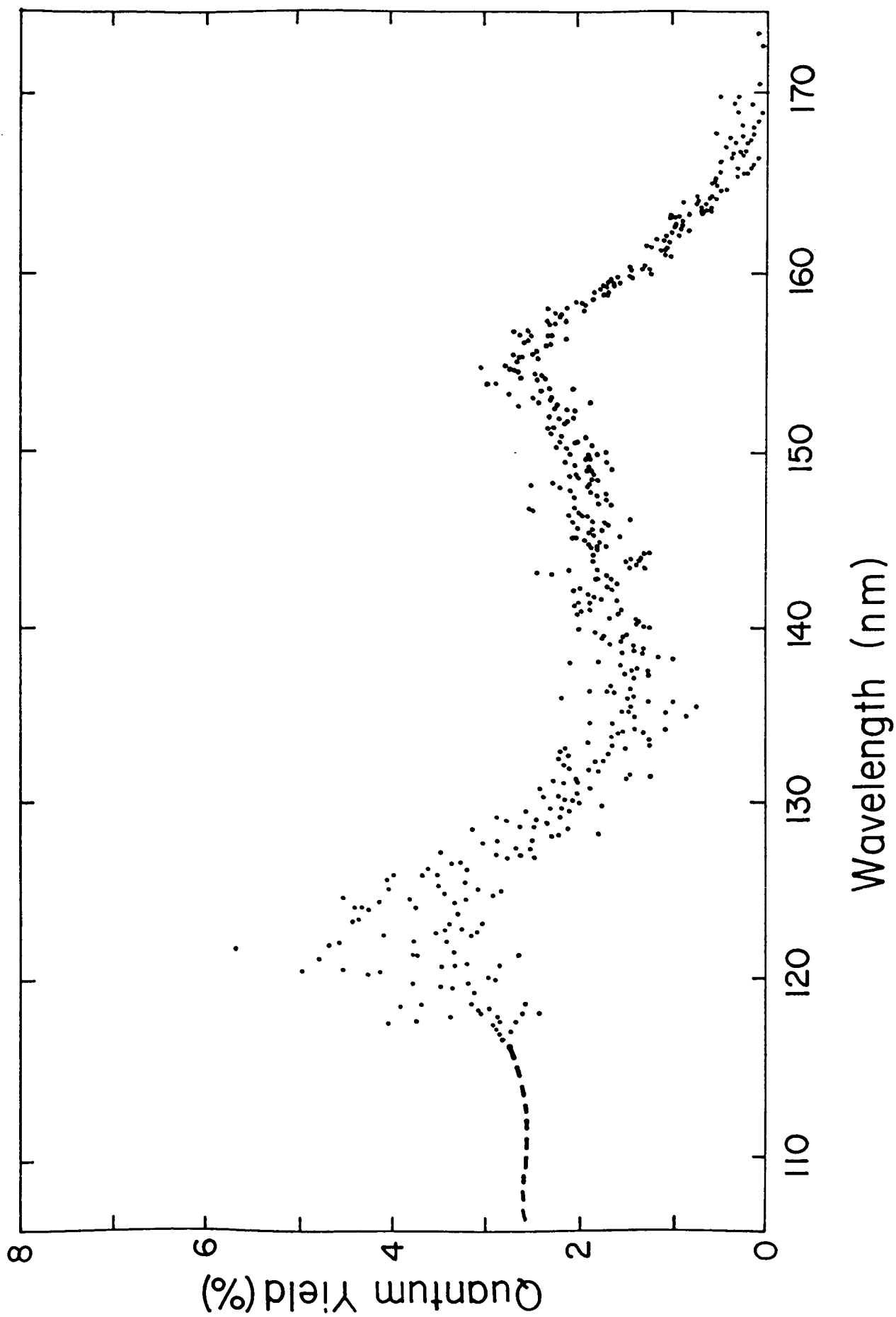


Fig. 2

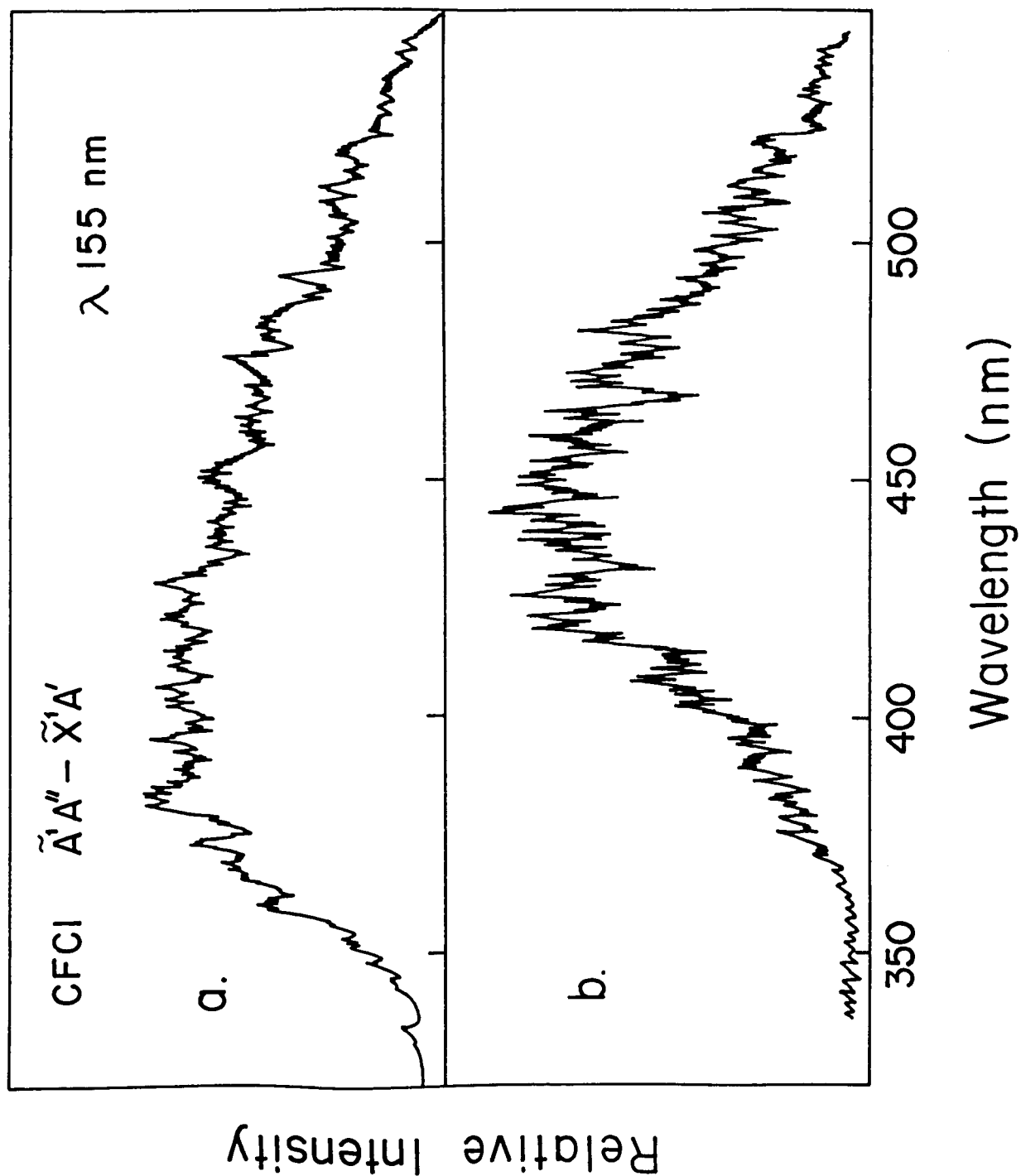
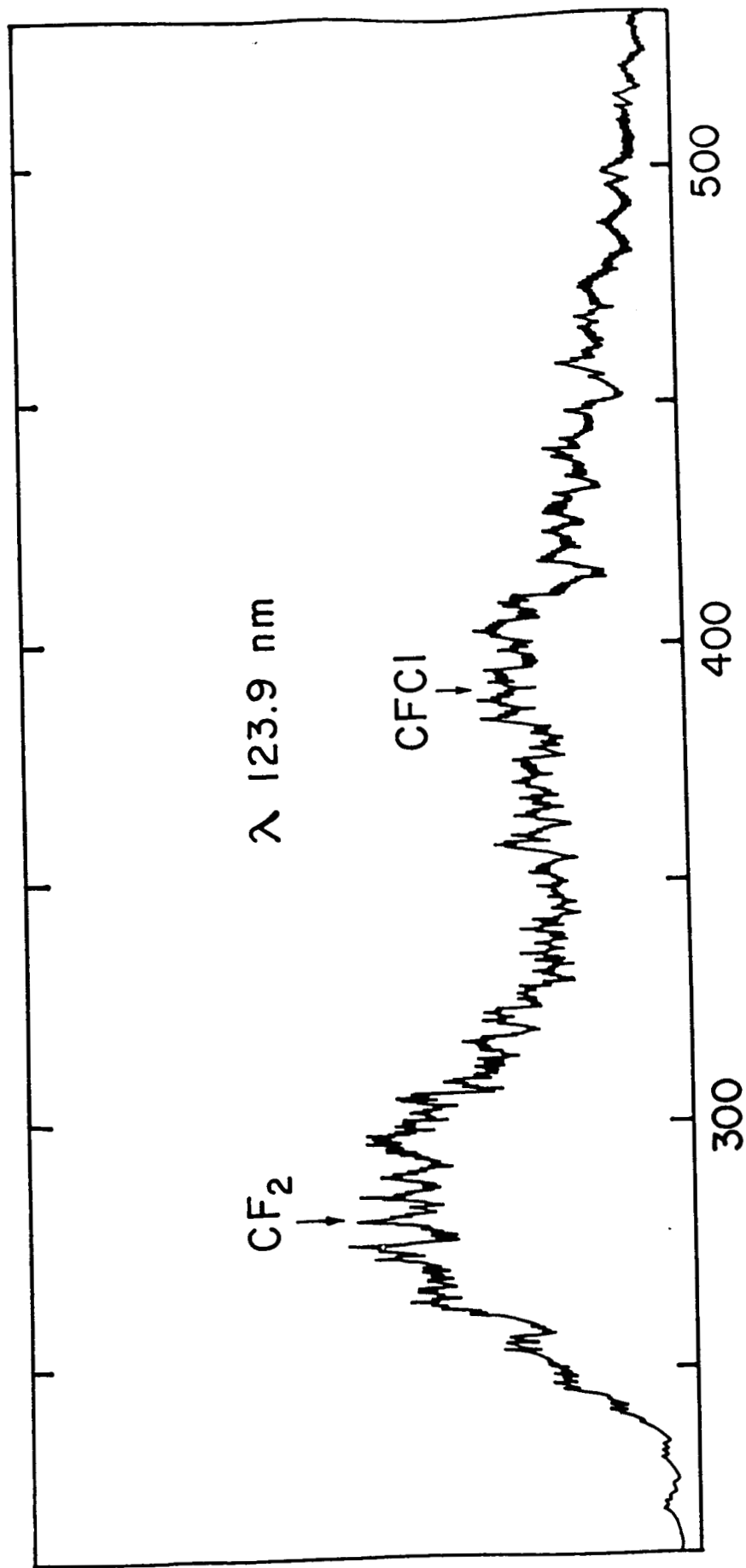


Fig. 3

Relative Intensity



Wavelength (nm)