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Quantitative Studies for Photoabsorption and Fluorescence of HCl

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ABSTRACT

Photoabsorption and fluorescence cross sections of HCl are investigated in the wavelength region between 105-220 nm. The oscillator strengths of discrete structures at wavelengths shorter than 130 nm arc measured.

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I. INTRODUCTION

The absorption spectrum of HCl was analyzed first by Price[1] in the early thirties. Spectroscopic investigations have been done recently by Ginter, Tilford, and their colleagues[2,3,4] and by Doulgas and Greening.[5] Jacques and Barrow[6] have studied the emission features of HCl from the $B(V)^1\Sigma^+$ state. Absorption cross sections of HCl have been investigated by Myer and Samson,[7] Inn,[8] and Smith et al.[9] The work of Inn was in the wavelength region of 140-200 nm, which is caused by the absorption continuum of the $A^1\Pi \leftarrow X^1\Sigma^+$ transition. Smith et al.[9] carried out the measurement of accurate oscillator strength of the $C^1\Pi$ state. Myer and Samson[7] have measured the absorption cross sections in the 105-210 nm region. Generally speaking, the absorption cross sections in the 105-130 nm region have not been accurately determined, especially at wavelenghts below 120 nm region, where spectrum is very complex as indicated from the works of Refs. 2-5. Assignments of the many absorption features are still uncertain. A study by combining quantitative measurements of both absorption and emission could give some useful hints for understanding the nature of higher states of HCl.

In addition to the interest in spectrosopy, the quantitative data of HCl are important for the studies of planetary atmospheric chemistry and interstellar chemistry. The existence of chlorine atoms in the earth's stratosphere have generated great concerns in recent years for their relation to the balance of ozone at altitudes about 25 Km.[10] HCl is a stable molecule resulted from the chemical reactions involving species Cl and ClO. HCl has a long chemical lifetime in the stratosphere, and only chemical reactions (mainly with OH) and photodissociation can destroy it. In addition to the existence in the earth's atmosphere, HCl has also been found in the stratosphere of Venus, whose photo-

chemistry has been discussed.[10] In the interstellar medium, HCl has been predicted to exist in clouds containing both hydrogen and chlorine species,[11] however, so far the existence of HCl has not been confirmed by observation. It is likely that HCl is destroyed by photodissociative process occuring in the interstellar diffuse clouds. The quantitative photoabsorption and fluorescence data are thus needed for determining the destruction rate of HCl in the interstellar medium.

II. EXPERIMENTAL

The set-up for this experiment is the same as our previous measurements.[12] In short, synchrotron radiation dispersed by a 1 m monochromator (McPherson 225) entered into a photoabsorption cell through a LiF window. The monochormatic light intensity was occasionally measured with a copper plate, but more often monitored by a photomultiplier tube (PMT) with a LiF window externally coated with sodium salicylate. Fluorescence signals produced from the photoexcitation of molecules were measured by two photomultiplier tubes, one has a cathode sensitivity in the VUV and another in the UV-visible wavelengths.

HCl gas was obtained from Matheson with a purity of at least 99.0%. No further purification was made for the experiment. The photoabsorption spectrum obtained from the measurements did not show any absorption features caused by the most possible impurities such as O_2 or CO_2. The gas in the absorption cell was slowly pumped with a sorption pump at constant flow rate and pressure. A MKS Baratron (Model 310 CH) was used to measure the pressure. All data including synchrotron electron beam current, gas pressure, absorption signal, fluorescence signals were processed by an IBM personal computer.

III. RESULTS AND DISCUSSION

1. Photoabsorption Cross Section

The photoabsorption cross section of HCl was measured over the 105-200 nm wavelength region. The absorption cross section was determined by comparing light intensities with and without gas attenuation. The results are shown in Figs. 1-3. The previous studies have shown that the absorption spectrum for $\lambda < 120$ nm consists of sharp structures. Since the resolution of the monochromator we used (0.08 nm) is much larger than the line width of the absorption structure, our measurement only gives an averaged cross section over the monochromator bandwidth.

The absorbances measured at several absorption peaks do not vary linearly with the HCl pressure. This may be due to saturation of sharp absorption lines existing within the peak. The absorption cross section of the sharp lines may be so high that they totally absorb the light even at very low pressure, and further increase of HCl pressure would not attenuate the light intensity any further. Since a linear dependence of the absorbance on pressure was observed at the continuum (e.g. 115 nm), the saturation is definitely not caused by the formation of dimer. To minimize the saturation effect, the experimental cross sections were measured at low concentrations, normally $(3\text{-}5)\times10^{13}$ cm^{-3}. The measured values shown in Figs. 1-3 should be considered as the lower limits because of the saturation effect. Nevertheless, the absorption cross sections at the continuum are quite accurate, whose experiment uncertainties are estimated to be within 10% of the given values.

The band origins, ν_o, of various excited states of HCl have been given by Ginter and Ginter[4] and by Douglas and Greening.[5] In general, the positions of ν_o do not coincide with the absorption peaks, but usually within 0.3 nm

The assignment of the absorption peak shown in Figs. 1-2 is based on the ν_o value that is found nearby the peak and on the absorption strength which is comparable with the value given by Douglas and Greening.[5] Only the strong absorption peaks are labeled in Figs. 1-2 in order to avoid any ambiuity caused by the mixture of weak absorption peaks.

Oscillator strength can be calculated from absorption cross sections according to the following formula

$$F = 113 \int \sigma d\lambda / \lambda^2$$

with λ in $\mathring{A}$ and σ in Mb(10^{-18} cm^2). Oscillator strengths for the absorption peaks given in Figs. 1 and 2 are calculated as shown in Table 1. Compared with the data of Smith et al.[9], our oscillator strength for the $C^1\Pi(v'=0)$ state is low. However, for the higher v' states the agreement is reasonably good.

The absorption cross sections at wavelengths longer than 135 nm (corresponding to the $A^1\Pi \leftarrow X^1\Sigma^+$ transition) are shown in Fig. 3. At wavelengths between 135 and 170 nm, our measured cross sections range from 10 to 20% lower than Inn's.[8] The largest discrepancy occurs at the absorption peak around 155 nm. However, a good agreement is found for wavelengths longer than 170 nm. The strong dissociative nature of the $A^1\Pi$ state is responsible for the most photodissociative HCl in the atmospheres of earth and Venus. However, in the earth's stratosphere, photodissociation of HCl is not a significant loss process compared with the reaction of OH + HCl, because of the low absorption cross section at wavelengths longer than 180 nm where the O_2 transmission window starts.

2. Fluorescence

The emission of HCl from the electronic state B(or V)$^1\Sigma^+$ has been reported by Jacques and Barrow.[6] We have measured the fluorescence cross section of HCl

with a UV-visible PMT. No fluorescence signals have been detected with the solar blind PMT (response in 115-200 nm). Both the fluorescence and absorption cross sections were measured simultaneously at a monochromator resolution of 0.3 nm. The results are shown in Fig. 4.

The fluorescence signals can be expressed analytically as

$$I_f = C \cdot \sigma_f \, n e^{-n \cdot \sigma \cdot \ell} \frac{1}{1+\tau k n}$$

where C is the constant relating to geometric factors and detector efficiency, σ_f is the fluorescence cross section, n is the concentration of HCl molecule, σ is the total absorption cross section, ℓ is the optical path length from entrance to the PMT view region, τ is the radiative lifetime of the electronically excited state of HCl. The term of $\tau k n$ is small at low pressure. By comparing with the OH(A → X) photofragment fluorescence from photodissociation of water vapor, the cross section σ_f in Eq. 1 can be obtained. The fluorescence cross sections were measured at HCl concentrations around $(1\text{-}3)\times10^{14}$ cm^{-3}.

The fluorescence observed in the UV-visible region is mostly produced at excitation wavelengths shorter than 120 nm as shown in Fig. 4. The excited state may also fluoresce at wavelengths shorter than 115 nm through the resonance scattering process. However, our VUV PMT has a MgF_2 window which does not respond at wavelenghts shorter than 115 nm. The fluorescence we detected mainly results from transitions between the excited upper states and an intermediate excite state (most likely the $A^1\Pi$ state). For the excitation wavelengths in the 115-120 nm region, the fluorescence is mainly due to the B(or V)$^1\Sigma^+$ state, whose emission is known to be in the 200-300 nm region.[6]

Fig. 4 shows several states that emit, these including $H^1\Sigma^+$ and $M^1\Pi$. The quantum yields are low for these two states compared with the $V^1\Sigma^+$ state. These states are likely to be strongly dissociative.

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TABLE 1

Oscillator Strength for Strong Absorption Bands of HCl

State	λ(nm)	Δλ(nm)	$\sigma_p(10^{-18}cm^2)$	f	f (ref. 9)
$b^3\Pi_1(v^1=0)$	133.2	0.6		0.0026	
$v^1=1$	128.6	0.4		0.0068	
$v^1=2$	124.4	0.4		0.0026	
$v^1=3$	120.7	0.4		0.0013	
$H^1\Sigma^+(v^1=0)$	112.8	0.5	35	0.0068	
$K^1\Pi(v^1=0)$	111.6	0.5	61	0.015	
$M^1\Pi+H^1\Sigma(v^1=1)$ (unresolvable)	110.4	0.5	126	0.027	
$j^3\Sigma-(v^1=0)$	111.9	0.2	16	0.0029	
$N^1\Pi(v^1=0)$	111.1	0.2	11	0.0020	
$m^3\Pi(v^1=0)$	111.0	0.1	16	0.0015	
$j^3\Sigma^-(v^1=1)$	109.3	0.4	16	0.0061	
$r^3\Pi(v^1=0)$	109.	0.4	19	0.0072	
$K^1\Pi(v^1=1)$	108.4	0.3*	18	0.0052	
$R^1\Pi(v^1=0)$	108.2	0.3*	22	0.0064	
$m^3\Pi(v^1=1)$	107.7	0.2*	34	0.0066	
$H^1\Sigma^+(v^1=2)$	107.6	0.2*	28	0.0055	
$M^1\Pi(v^1=1)$	107.3	0.2*	21	0.0041	
$C^1\Pi(v^1=0)$	129.0	0.8*	515	0.10	0.185
$(v^1=1)$	124.9	0.7	88	0.0184	0.022
$(v^1=2)$	121.0	0.3	13	0.003	

*estimated

Δλ: bandwidth, σ_p: peak absorption cross section, f: oscillator Strength calculated with $f = 113\int\sigma d\lambda/\lambda^2$

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FIGURE CAPTIONS

Fig. 1 Photoabsorption Cross Sections of HCl at 105-120 nm. The dotted line at 110.4 nm indicates the shape of the absorption band.

Fig. 2 Photoabsorption cross sections of HCl at 120-130 nm. The dotted lines at 124.5 and 129 nm indicate the shape of the absorption bands.

Fig. 3 Photoabsorption cross sections of HCl at 135-200 nm.

Fig. 4 Spectra of photoabsorption cross section (full line)and and fluorescence cross section (dotted line) of HCl measured at a monochromator of 0.3 nm.

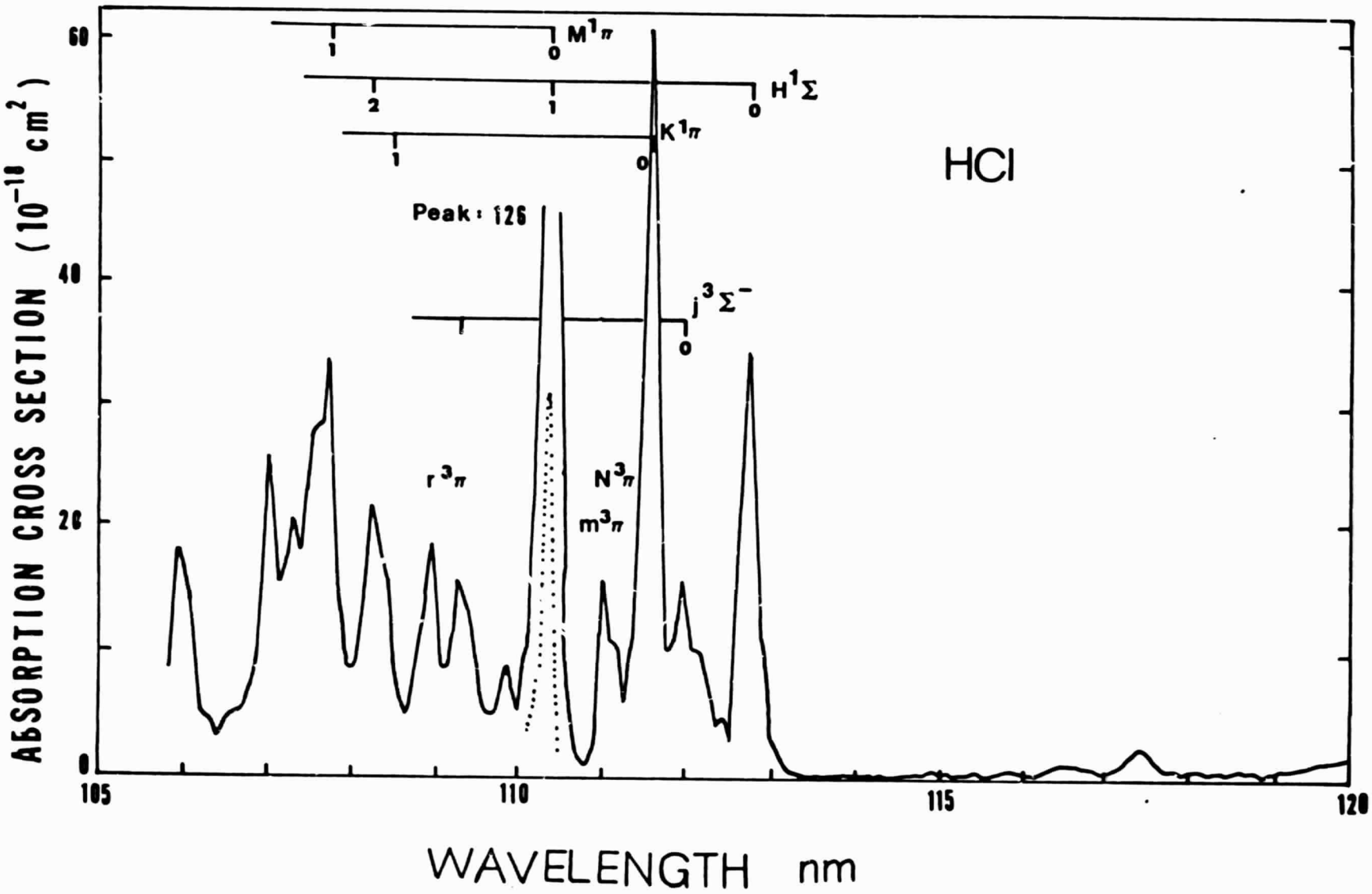
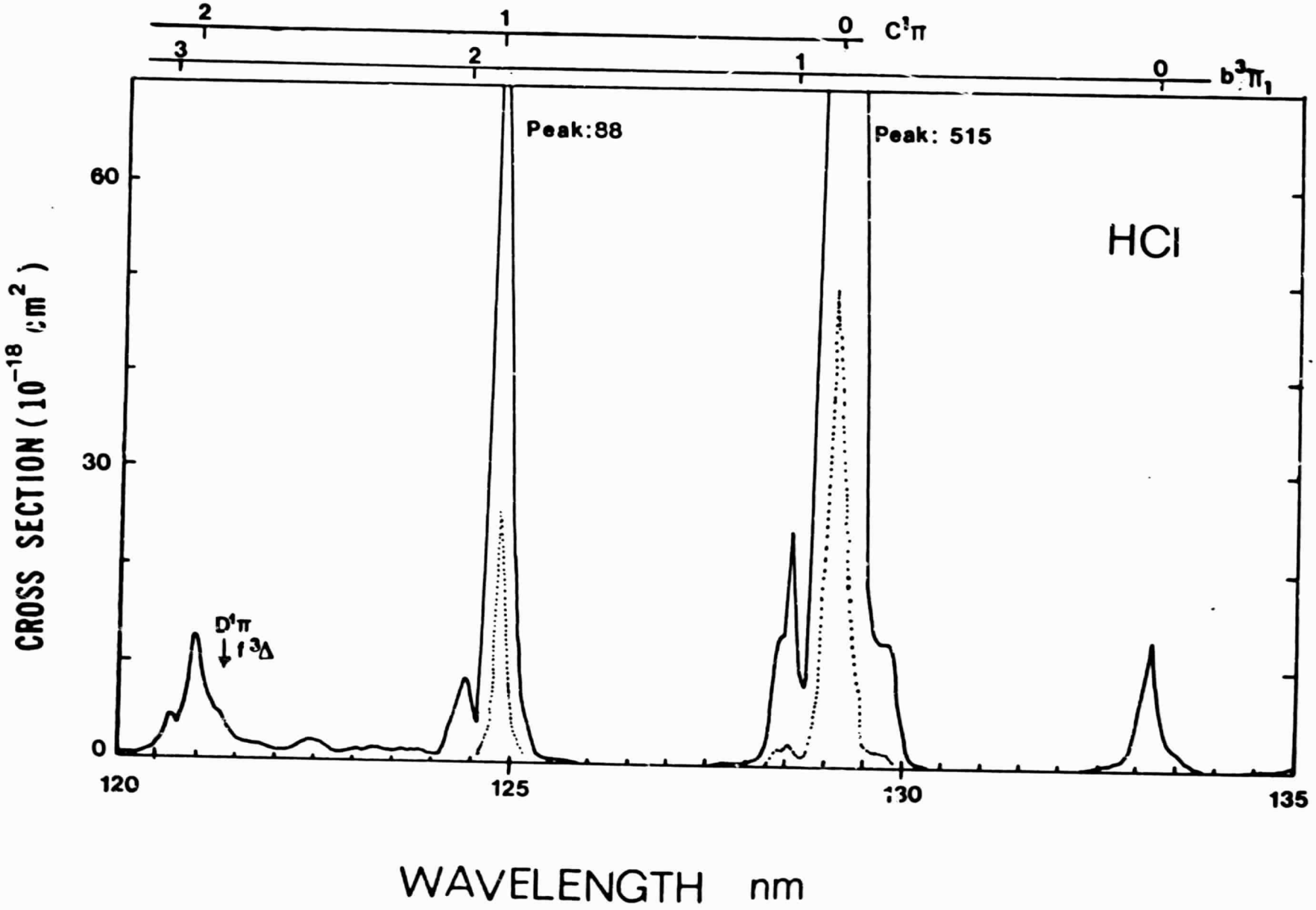
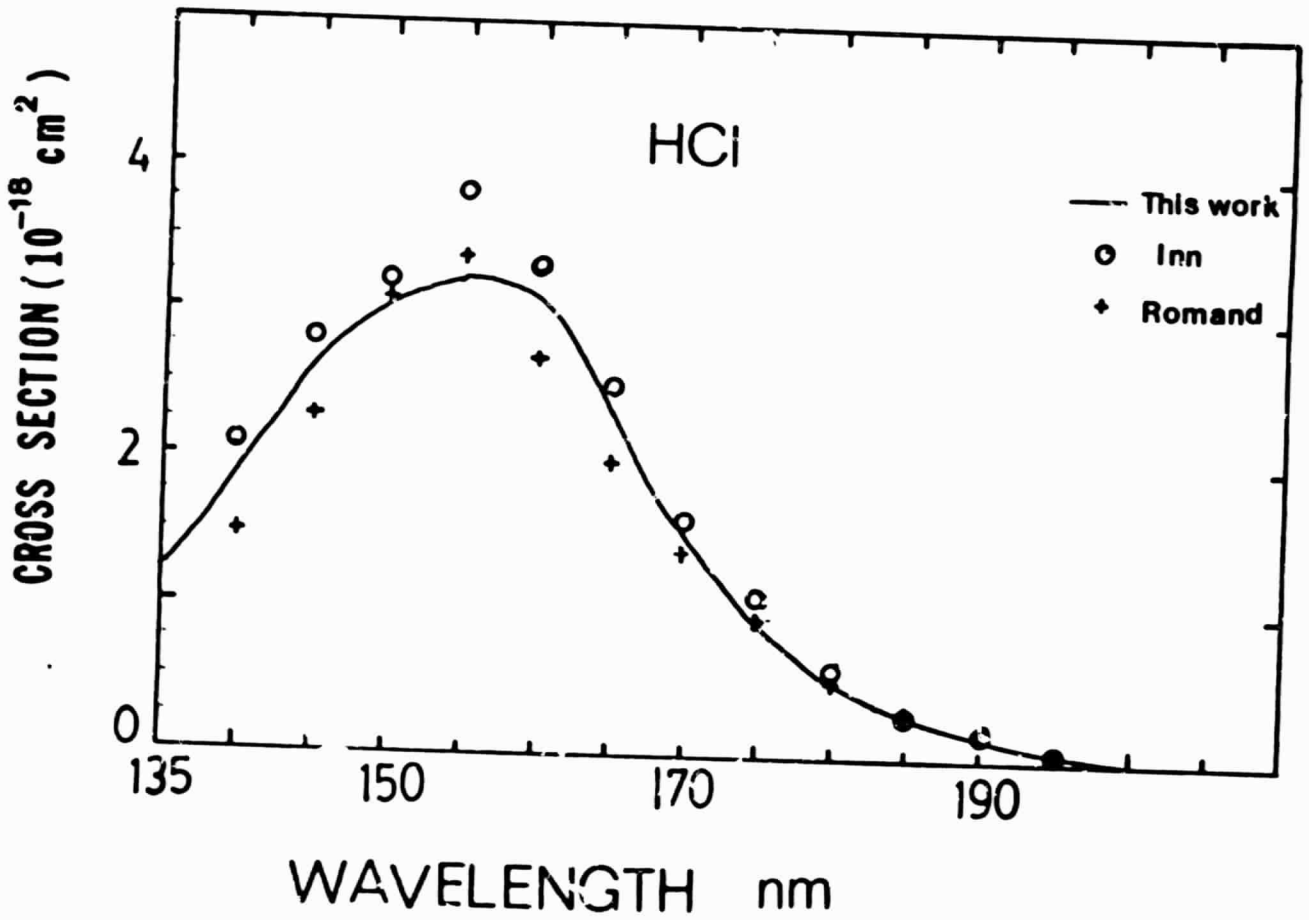

HCl
ABSORPTION CROSS SECTION (10^{-18} cm^2)
WAVELENGTH nm
Peak : 126
$M^1\pi$
$H^1\Sigma$
$K^1\pi$
$j^3\Sigma^-$
$r^3\pi$
$N^3\pi$
$m^3\pi$
60
40
20
0
105
110
115
120

Fig. 1


2
1
0
C¹π
3
2
1
0
b³π₁
Peak:88
Peak: 515
HCl
60
30
0
CROSS SECTION (10^{-18} cm^2)
D¹π
↓ f³Δ
120
125
130
135
WAVELENGTH nm


HCl
CROSS SECTION (10^{-18} cm^2)
WAVELENGTH nm
This work
Inn
Romand
0
2
4
135
150
170
190

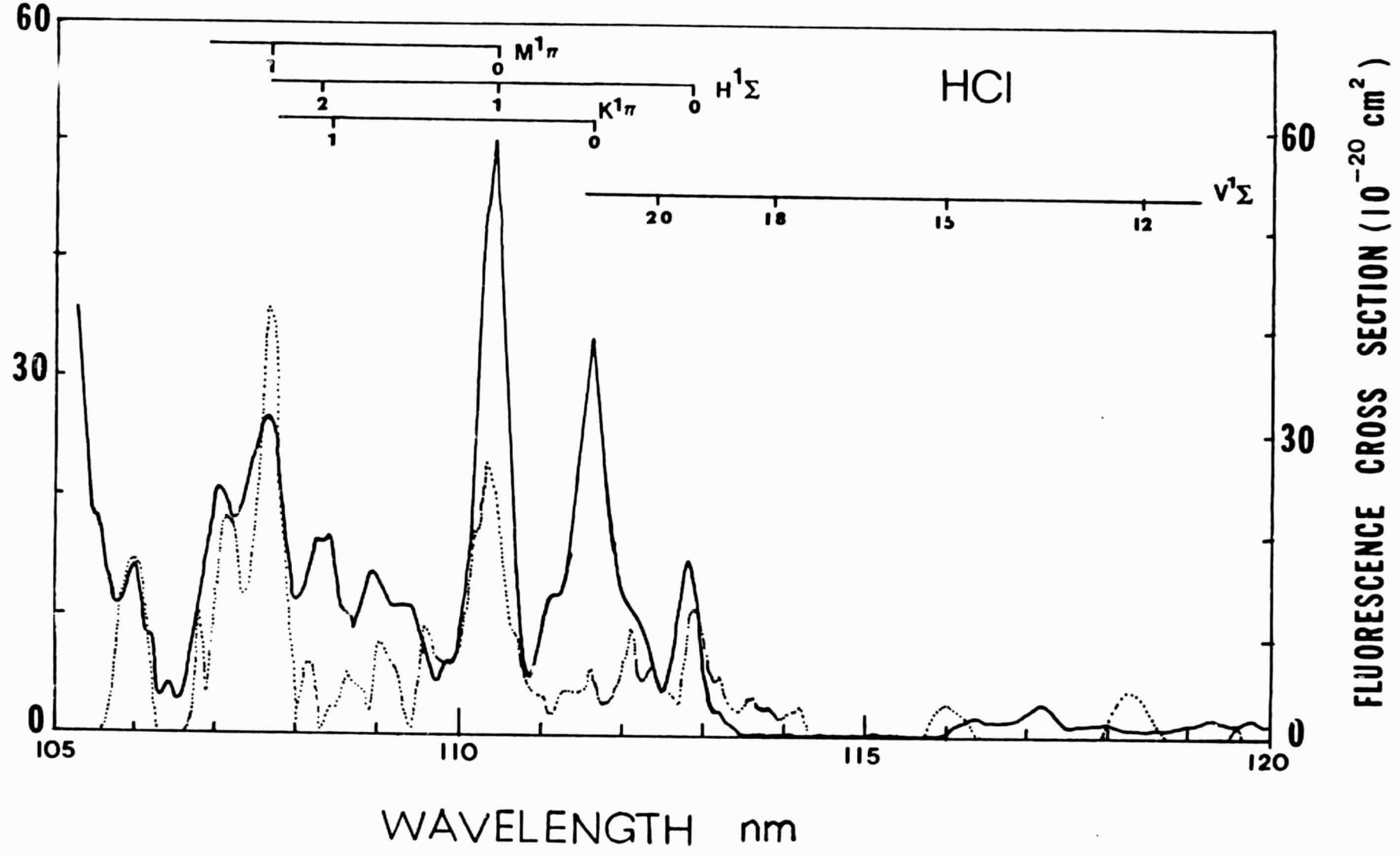

HCl
M¹π
H¹Σ
K¹π
V¹Σ
ABSORPTION CROSS SECTION (10⁻¹⁸ cm²)
FLUORESCENCE CROSS SECTION (10⁻²⁰ cm²)
WAVELENGTH nm
60
30
0
105
110
115
120

Fig. 4