

VACUUM UV FLUORESCENCE EXCITATION SPECTRUM OF ICl USING SYNCHROTRON RADIATION

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Summary

The fluorescence excitation spectrum of ICl in the region 160 - 200 nm has been recorded using tunable synchrotron radiation. The dominant absorption features in this region involve transitions to Rydberg states but the main fluorescence (for $\lambda \geq 200$ nm) is from ion pair states.

1. Introduction

Until quite recently very little was known about the ion pair states of halogen and interhalogen molecules. However, there has been considerable recent interest following the discovery that they have rather unusual chemical and spectroscopic properties [1 - 10].

From a chemical viewpoint they are of interest because of their high reactivity [1 - 4]; they are known to react with noble gas atoms [4] and to be capable of breaking some of the strongest chemical bonds (*e.g.* the carbon-fluorine bond) [3]. From a spectroscopic viewpoint, ion pair states are of interest because of the extensive oscillatory continuum emission to which they generally give rise [5 - 10].

We have previously reported [2, 7 - 10] work on the ion pair states of I₂, IBr and Br₂. However, despite considerable efforts we have, until now, failed in attempts to excite the ion pair states of ICl using single-photon techniques. In previous attempts we have used an ArF laser (193 nm), a commercial fluorometer ($\lambda \geq 190$ nm), an intense mercury lamp (184.9 nm) and an F₂ laser (157 nm). These failures surprised us in view of the relative

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ease with which the other halogen ion pair states could be excited and we therefore decided to make a systematic fluorescence excitation study using tunable synchrotron radiation. This study has revealed that the most intense fluorescence results from excitation between 160 and 180 nm, which is a region poorly covered by conventional line sources. Our work serves to illustrate the very great advantages associated with using a continuously tunable synchrotron radiation source.

2. Experimental details

All experiments were carried out using beam line 12 at the Science and Engineering Research Council Daresbury Synchrotron Source. Radiation from the storage ring was dispersed using a Spex 1500 SP Czerny–Turner monochromator. Samples of ICl were contained in conventional Spectrosil fluorescence cells (cross section, 1 cm²) fitted with a greaseless tap. These cells were then mounted in an evacuable chamber which allowed absorption and fluorescence spectra to be monitored simultaneously. Absorption spectra were recorded using a screen coated with sodium salicylate to convert vacuum UV radiation to wavelengths suitable for monitoring with a conventional photomultiplier (EMI 6256B). Undispersed fluorescence was monitored at right angles to the excitation beam using a quartz-windowed photomultiplier (Mullard PM2020Q) outside the evacuable box (*i.e.* fluorescence was observed for 650 nm \geq λ \geq 185 nm).

3. Results

The absorption spectrum of ICl in the region 160 - 200 nm is shown in Fig. 1. The two sets of Rydberg bands previously reported by Venkateswarlu [11] are clearly seen between 190 - 180 nm and 175 - 165 nm. The sloping background on which the strong Rydberg peaks are superimposed is due mainly to the change in monochromator throughput I_0 with wavelength.

The absorption spectra of Cl₂ and I₂ were also recorded, for comparison, as ICl exists in equilibrium with both these molecules. Cl₂ does not show any structured absorption in this region; however, I₂ exhibits strong Rydberg absorption below 175 nm. Thus, in order to suppress I₂, excess Cl₂ was added to all samples of ICl.

A fluorescence excitation spectrum of ICl, in the region 159 - 195 nm, is shown in Fig. 2. The most intense fluorescence is observed for excitation between 172.5 and 182.5 nm. The banded structure observed between 180 and 189 nm and between 170 and 175 nm is due to absorption by ICl (absorption by ICl strongly reduces the intensity of the excitation beam before it traverses the region from which fluorescence is observed, *i.e.* the sample is optically thick). This point has been confirmed by running spectra at lower pressures of ICl; as the pressure of ICl is reduced the sample becomes

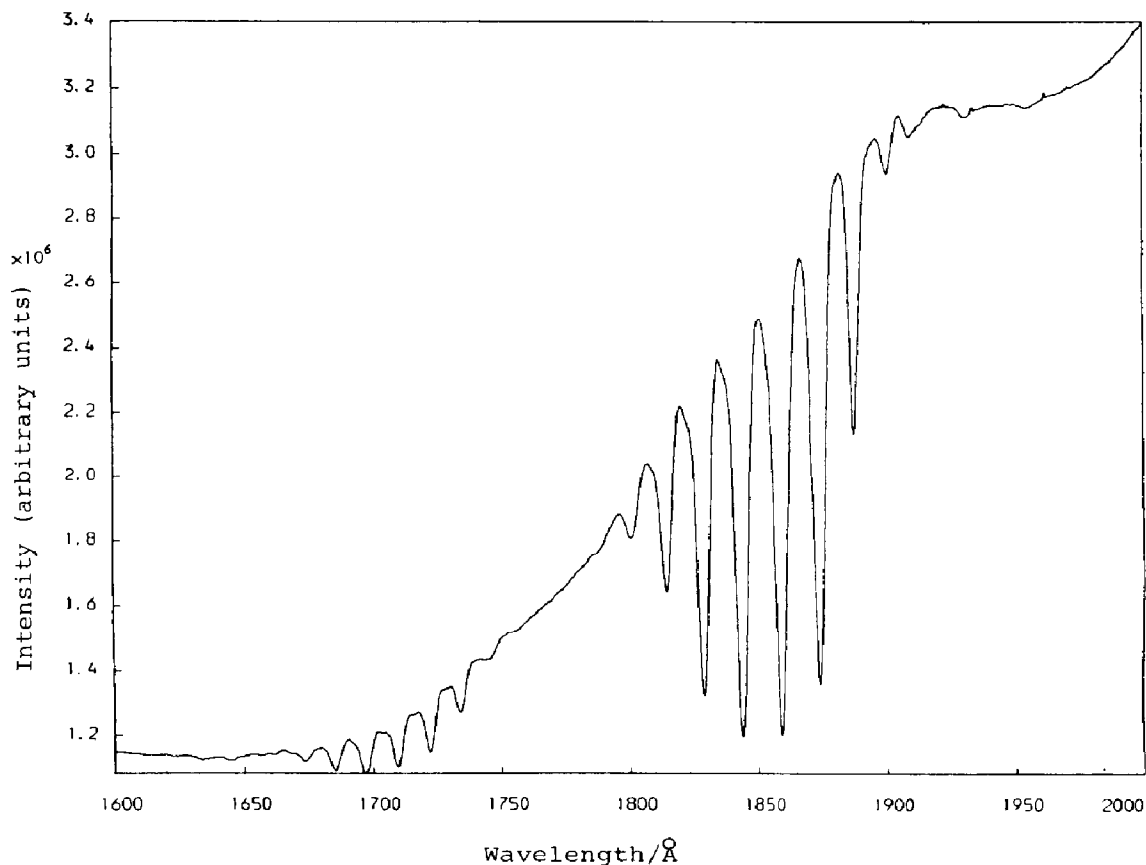


Fig. 1. Vacuum UV absorption spectrum of ICl ($P_{\text{ICl}} = P_{\text{Cl}_2} = 268 \text{ N m}^{-2}$; path length, 1 cm; resolution, 3 Å).

optically thin and the banded structure becomes much weaker relative to the fluorescence. The structure observed between 174 and 178 nm persists even at low pressures of ICl and is therefore not due to optical thickness of the sample.

There is a distinct break in the fluorescence excitation spectrum between 171 and 168 nm with a second highly structured system observed below 168 nm down to the limit of the Spectrosil-quartz cut-off (160 nm). It should be noted that the spectrum shown in Fig. 2 has not been corrected for the change in incident light intensity with wavelength: this is approximately 30% less below 168 nm compared with that at 175 nm. Thus the peak intensity for the fluorescence system below 168 nm is approximately equal to that of the peak at 175 nm. The second fluorescence excitation system appears to be quite sensitive to quenching by ICl and/or Cl₂ since the intensity of this system, relative to that at longer wavelengths, declines rapidly for halogen pressures above 133 N m⁻². The separation between the peaks corresponds to the vibrational frequency of the Rydberg states in this region; however, the *structure* in this region does not change with the partial pressure of ICl and is not therefore due to the effect of optical thickness.

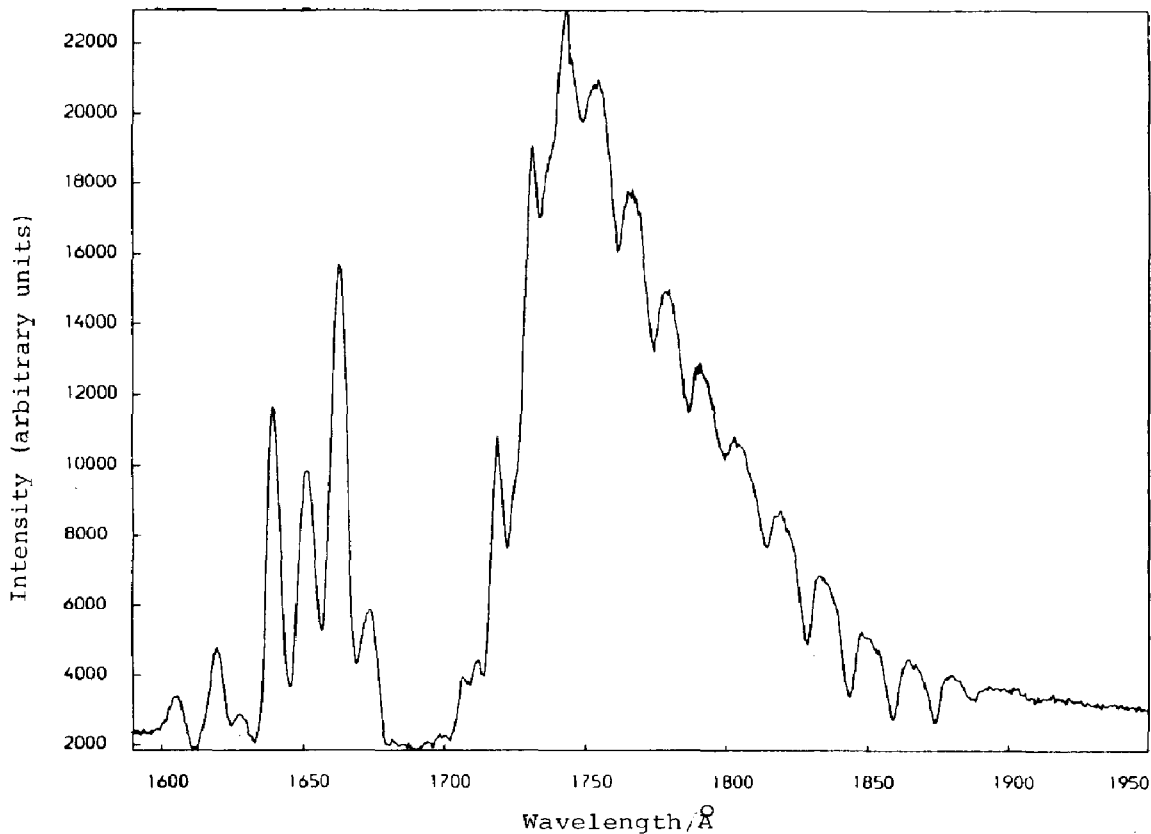


Fig. 2. Vacuum UV fluorescence excitation spectrum of ICl ($P_{\text{ICl}} = P_{\text{Cl}_2} = 133 \text{ N m}^{-2}$). The spectrum has not been corrected for the variation with wavelength of the incident light intensity.

Fluorescence excitation spectra were also recorded following the addition of N_2 as a quenching gas up to a total pressure of 12 kN m^{-2} . As the pressure of N_2 was increased the total fluorescence intensity (for excitation wavelengths between 160 and 190 nm) also initially increased up to about $8 \text{ kN m}^{-2} \text{ N}_2$, after which the intensity decreased. In these experiments no attempt was made to disperse the fluorescence and thus the photomultiplier registered emission from both the initially populated states and any other states populated during collisional cascade processes [10], provided that these states emitted in the region 185 - 650 nm. However, the intensity increase was not uniform and the bands between 160 and 170 nm increased in intensity more rapidly than the broad system at longer wavelengths (Figs. 2 and 3 should be compared). Furthermore, the relative intensities of some of the bands within the 160 - 170 nm system changed with pressure and there appear to be at least two electronic systems which behave differently in this region.

The increase in total fluorescence (about 30%) with increasing pressure of N_2 is probably due to pressure broadening of the absorption spectrum.

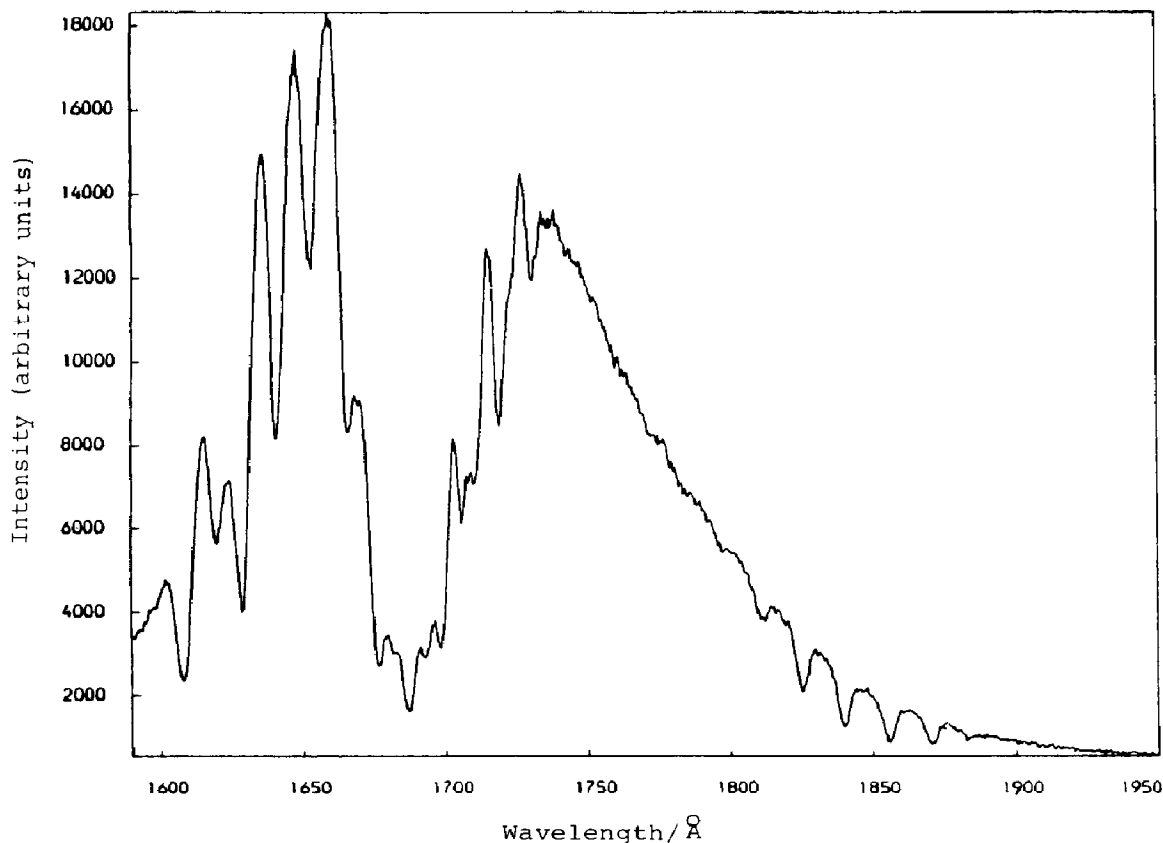


Fig. 3. Vacuum UV fluorescence excitation spectrum of ICl in the presence of a large excess of N_2 ($P_{ICl} = P_{Cl_2} = 133 \text{ N m}^{-2}$; $P_{N_2} = 12.3 \text{ kN m}^{-2}$). The spectrum has not been corrected for the variation with wavelength of the incident light intensity.

This has been observed previously with I_2 where the effect has been studied in some detail [12].

By comparison with previous work on halogen ion pair states [2, 4, 8, 10] we would expect collisions with N_2 to induce efficient interstate transfer and cascading with the eventual population of the lowest state within the ion pair manifold; this state would then be expected to radiate to lower valence states.

4. Discussion

It is clear from this study that the Rydberg states, which dominate the absorption spectrum of ICl in the region 165 - 190 nm, do not give rise to fluorescence at $\lambda \geq 190 \text{ nm}$, as the excitation spectrum does not exhibit the structure observed in absorption. The spectra reported by Venkateswarlu [11] suggest that these Rydberg states are predissociated. No rotational structure is observable in the published spectra; however, it is still possible for discrete structure to exist close to some of the band origins, where the

rotational structure is dense and difficult to resolve. Our results show clearly that the first Rydberg system is completely predissociated and that this is probably also the case for the second Rydberg system. Fluorescence from this second system could occur below our detection limit and some doubt therefore remains as to whether or not fluorescence can take place from this second system.

The structure observed on the second fluorescence excitation system (160 - 170 nm) suggests that the upper state is a Rydberg state. However, Venkateswarlu [11] has reported a strong and densely structured absorption system in this region which must be due to an upper ion pair state; unfortunately no analysis of this spectrum was given. It would appear that the ion pair state is strongly perturbed by a close-lying Rydberg state and that interference between the two states results in the pronounced structure observed in the fluorescence excitation spectrum. The intensity changes observed when N_2 is added as a quenching gas also suggest that more than one electronic state is involved in this region.

Several ion pair states are known in the region of interest [13] and transitions to two of these states (0^+ and 1) in the lowest cluster, correlating with $I^+(^3P_2)$ and $Cl^-(^1S_0)$, are fully allowed. Both states are expected to lie close in energy to one another and, as a result of the large change in equilibrium internuclear separation between the ground state and the ion pair states, high vibrational levels should be populated in the absorption process. The fluorescence is therefore expected to be predominantly of the bound free type (*i.e.* oscillatory continuum fluorescence). Further work to examine the dispersed fluorescence is therefore desirable and the present work shows that excitation could be achieved using the atomic lines of nitrogen at 174 nm.

5. Conclusions

We have recorded the first fluorescence excitation spectrum of ICl in the vacuum UV and have shown that at least three upper states are involved in the fluorescence. These states all show behaviour characteristic of ion pair systems; however, the states excited in the region 160 - 170 nm probably have mixed Rydberg and ion pair parentage. Further work, at higher resolution, on the absorption spectrum of ICl in the vacuum UV, together with work on the dispersed fluorescence, is clearly desirable.

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