# ULTRA-VIOLET EMISSION SPECTRA OF XENON AND KRYPTON FLUORIDES

S. L. N. G. KRISHNAMACHARI, N. A. NARASIMHAM AND MAHAVIR SINGH

*Spectroscopy Division, Atomic Energy Establishment, Trombay, Bombay*

## INTRODUCTION

IN June 1962, Neil Bartlett[1] of the University of British Columbia reported a reaction of xenon with platinum hexafluoride. This was later confirmed by Claassen *et al.*[2] at the Argonne National Laboratory who further established that the rare gas xenon reacted directly with fluorine. Immediately afterwards a number of xenon fluorides, *viz.*, $XeF_4$, $XeF_2$, $XeOF_4$ were prepared and identified. Soon after, krypton also was found to form fluorides, though much less readily.[4] These discoveries stimulated great interest in the chemistry of rare gases which were hitherto supposed to be absolutely inert. During the course of our investigations on the emission spectra obtained in discharges through $BF_3$ in the presence of xenon and krypton, we have obtained certain spectral features in the region 2200 Å to 3500 Å which are attributable to fluorides of xenon and krypton. Results of these investigations are briefly presented in this report.

## EXPERIMENTAL

An electrodeless discharge through mixture of $BF_3$ and xenon excited by means of a micro-wave oscillator (frequency 2,450 Mc./sec.) gave two intense groups of bands at 3510 Å and 3080 Å and two relatively weaker ones at 2635 Å and 2355 Å (Fig. 1). So far as we could ascertain, these bands do not belong to any of the known band systems. The spectra of BF, BO and $BO_2$ molecules were also obtained in these discharges ; however, they do not interfere with the above bands and further by adjusting the experimental conditions they could be largely suppressed. The bands could be obtained with equal ease when $BF_3$ was replaced by LiF or NaF. However, since these are solids, it was found necessary to heat them in the discharge tube initially to about 300° C.

There was no enhancement of the intensity of these bands when oxygen was introduced into the system. The most favourable condition was found to be that when the pressure of xenon in

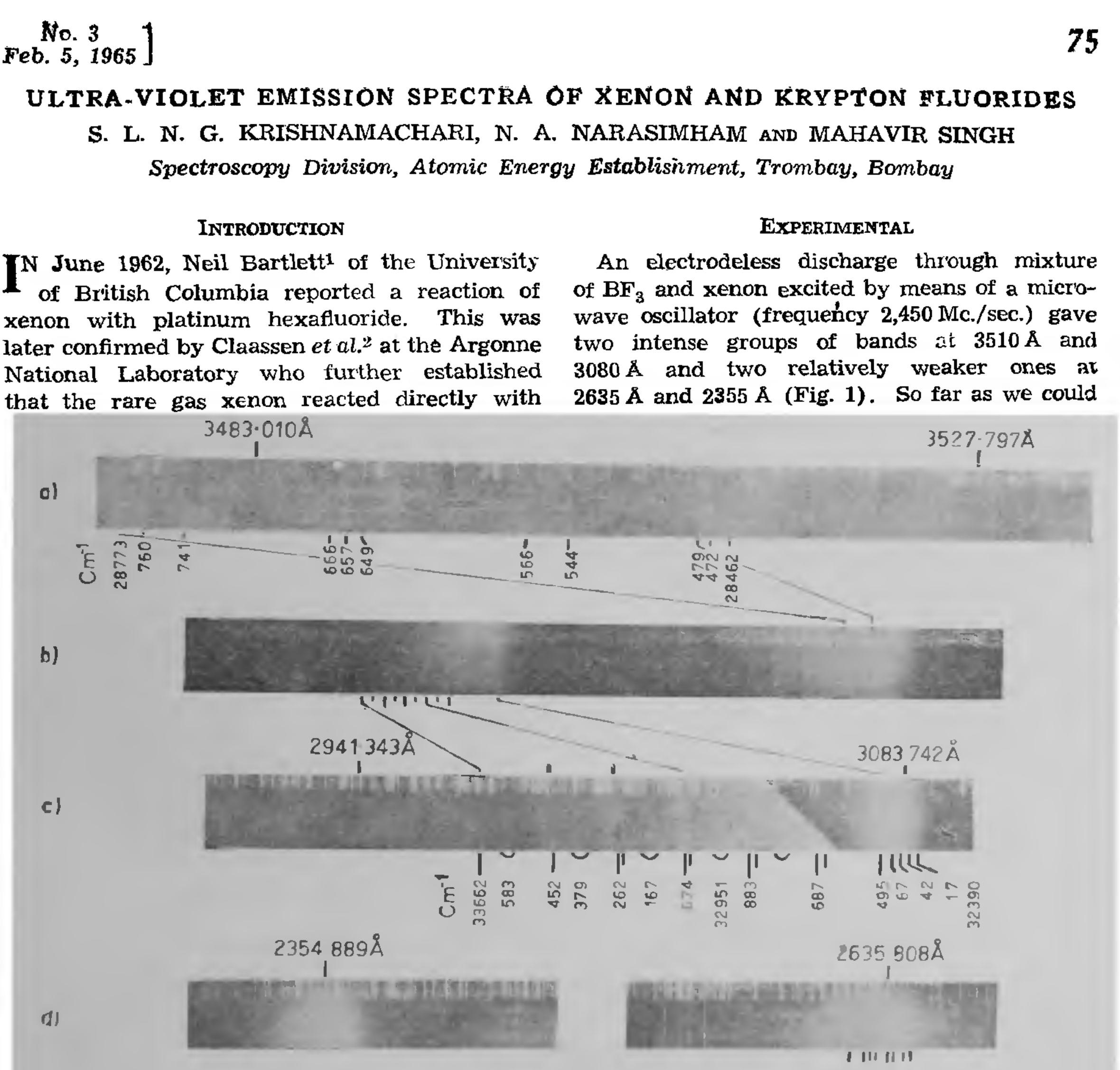


FIG. 1. Emission bands obtained in discharges through Xenon and LiF. (*a*) 3510 Å band recorded in the second order of 6·6 metre concave grating spectrograph. (*b*) 3080 Å and 3510 Å bands recorded on a Hilger medium quartz spectrograph. (*c*) 3080 Å band recorded on a Bausch and Lomb large quartz spectrograph. (*d*) 2635 Å and 2355 Å bands recorded on a Hilger medium quartz spectrograph.

the discharge tube was about 10–15 cm. and the discharge was in the form of streaks.

During preliminary studies, the spectra were recorded on Hilger quartz spectrographs of small and medium dispersions. Since the bands at 3510 Å and 3080 Å are the more intense ones in each group, they are photographed at higher dispersion. Figure 1 (*a*) represents part of the 3510 Å band taken in the second order of the 6·6 metre concave grating spectrograph at a dispersion of 0·55 Å/mm. while Fig. 1 (*c*) represents the 3080 Å band taken on a Bausch and Lomb large quartz spectrograph at a dispersion of 5 Å/mm. The weaker bands at 2635 Å and 2355 Å are photographed on a Hilger medium quartz spectrograph having a dispersion of 8 Å/mm. at 2500 Å.

Analogous experiments with krypton in place of xenon gave only two spectral features at 2485 Å and 2220 Å (Fig. 2).

about the same as that between the centres of the 3080 Å and 2355 Å bands (~ 10,000 cm.$^{-1}$). Furthermore this separation is rather close to the ground state doublet separation of the ionised xenon atom (10,537 cm.$^{-1}$) and appears to be significant.

(*a*) *Bands at 3510 Å and 2635 Å.*—The feature at 3510 Å is easily the most complex of all the bands observed. The most intense part of this band, when photographed on the 6·6 metre grating spectrograph, exhibits four groups of bands separated from one another by ~ 100 cm.$^{-1}$ Each of these groups appears to possess three to four well-marked heads. Reference to the Fig. 1 (*a*) will show that the band extends beyond 3510 Å with a structure which appears like the rotational fine structure of a band. Such a structure is also observable, though with lesser intensity, in all the four groups. At wavelengths lower than the last of these four groups, there

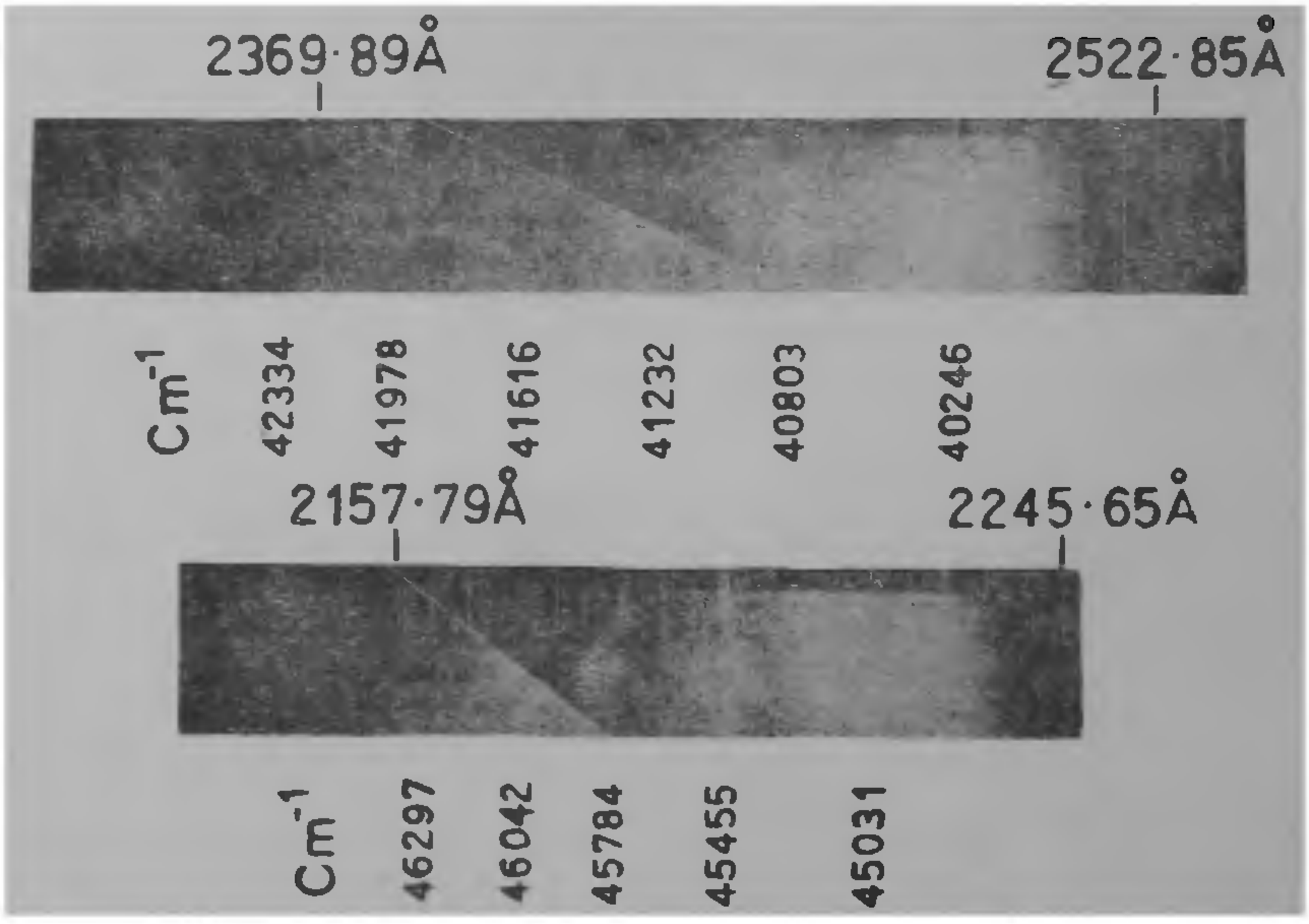


FIG. 2. Emission bands obtained in discharges through Krypton and LiF. (*a*) 2485 Å band and (*b*) 2220 Å band recorded on Hilger medium quartz spectrograph.

## RESULTS AND DISCUSSION

*I. Bands Associated with Xenon.*—From similarity in their intensity behaviour, the bands at 3510 Å and 2635 Å are considered to form one group and the 3080 Å and 2355 Å bands another group. It is interesting to note that when so grouped, the interval (~ 9500 cm.$^{-1}$) between the centres of the 3510 Å and 2635 Å bands is

are a few more weaker bands which probably form a progression but these, however, were not photographed in the high dispersion. The 2635 Å band is more diffuse but some eight or nine heads could be measured in its main body. These are shown marked in Fig. 1 (*d*). This band is also followed by a few much more diffuse and weak bands on the shorter wavelength side.

(b) *Bands at 3080 Å and 2355 Å.*—Under the resolution employed the 3080 Å band is seen to consist of an intense group of closely spaced heads with an average separation of $\sim 25$ cm.$^{-1}$ No further structure of these heads was revealed when the 6·6 metre grating spectrograph was used. This feature of the band appears very much similar to the K structure of a simple polyatomic molecule. This band is followed on the shorter wavelength side by a series of weak, diffuse bands. These could be grouped into two progressions of five or six bands each. One of these progressions consists of bands each of which shows a fairly sharp head followed by a weaker component on the longer wavelength side. These bands occur at separations of $\sim 192$ cm.$^{-1}$ The other progression consists of more diffuse bands having separations estimated to be $\sim 210$ cm.$^{-1}$ The first member of this progression that could be clearly seen on the plate is $\sim 300$ cm.$^{-1}$ from the main head at 3080 Å and lies towards its shorter wavelength side. The 2355 Å band is completely diffuse with no distinguishable features. The contour of the band however indicates a degradation towards shorter wavelength side. It is realised that no more satisfactory analysis of the 3080 Å band could be given. It is possible to regard the above progressions as arising from a series of excited vibrational levels belonging to the two rather similar modes of vibration of an upper electronic state to a lower electronic state of a practically repulsive nature. The diffuseness of the successive members of the progression seems to support this view. If one accepts for argument that the emitter of this band system is $XeF_2$, the infra-red and Raman data[5] for the ground state of this linear molecule being known to be $\nu_1 = 497$, $\nu_2 = 213$ and $\nu_3 = 555$ cm.$^{-1}$, the separations of 192 cm.$^{-1}$ and 210 cm.$^{-1}$ observed in the two series seem to correlate with the doubly degenerate bending frequency 213 cm.$^{-1}$

*II.—Bands Associated with Krypton*

In the discharge through krypton and LiF, two groups appear at 2485 Å and 2220 Å. Figure 2 shows these bands photographed on a Hilger medium quartz spectrograph. Here again the separation between the centres of the main heads of the 2485 Å and 2220 Å bands ($\sim 4800$ cm.$^{-1}$) is about the same as the doublet separation of the ground state of the krypton ion (5371 cm.$^{-1}$). Each of the two systems shows a progression of a diffuse pattern extending towards the shorter wavelength side. From the successive separation in each of the progressions vibrational frequencies of $\sim 425$ and $\sim 560$ cm.$^{-1}$ could be obtained corresponding to the two upper electronic states involved in the 2220 Å and 2485 Å systems respectively. Though these values happen to be close to two of the vibrational frequencies $\nu_1 = 449$,* $\nu_3 = 580$ cm.$^{-1}$ reported for $KrF_2$,[6] it is not certain how far the correlation would be justified.

Because of the current interest in such molecules it was thought useful to present the distinctive features of the spectra obtained, although the interpretations offered have to be considered provisional.

ACKNOWLEDGEMENT

The authors are very much indebted to Professor R. K. Asundi for his critical comments and valuable suggestions.

* Dr. Pimentel has intimated that this frequency of 449 cm.$^{-1}$ has been observed by Claassen *et al.* in the Raman spectrum of $KrF_2$

1. Bartlett, N., *Proc. Chem. Soc*, 1962, p. 218.
2. Claassen, H. H., Selig, H. and Malm, J. G, *J. Am. Chem. Soc.*, 1962, **84**, 3593.
3. Chernick, C. L., *et al.*, *Science*, 1962, **138**, 136.
4. *See* for example, Turner, J. J. and Pimentel, G. C., *Science*, 1963, **140**, 974.
5. Agron P. A., *et al. Ibid.*, 1963, **139**, 842.
6. Turner, J. J. and Pimentel, G. C. *Noble Gas Compounds*, Ed. Hyman, University of Chicago Press, 1963, p. 101. (A reprint of this paper has been kindly made available to us by Dr. Pimentel.)