Note on the Spectrum of Boron Fluoride

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The spectrum of boron fluoride was photographed in the first order of a 21-foot concave grating. Three new bands were found in the ultraviolet, the structure of which appears to be similar to that of the third positive bands of CO. The visible bands, most of which were known previously, are unlike those in the ultraviolet, having a very diffuse appearance.

VERY little is known of the spectrum of boron fluoride. Johnson and Jenkins[1] attempted to photograph it, but failed because of the presence of numerous SiF bands. Since then these experimenters have photographed and classified the bands of SiF, thus simplifying the difficulties involved in examining the bands of boron fluoride.

Since the boron fluoride molecule has the same number of electrons as N_2 and CO, its electronic structure should be similar to that of those molecules. Johnson and Tawde,[2] although they succeeded in photographing the boron fluoride spectrum with a Hilger E1 spectrograph, failed to find any resemblance between its bands and those of CO and N_2.

In the present investigation boron trifluoride was generated by treating a finely powdered mixture of calcium fluoride and boric anhydride with concentrated sulfuric acid. The gas was passed through a drying tube of phosphorus pentoxide, and through traps of fused sodium fluoride to remove hydrogen fluoride. A capillary discharge tube with nickel electrodes was used as a light source. Best results were obtained at a pressure of about 5 mm and with a current of 10 milliamperes. The photographs were taken with a 21-foot concave, Paschen mounted grating, having 14,000 lines per inch. Good first order plates were obtained, the dispersion being about 2.4–2.5A per millimeter, but the source was too weak to produce good second and third order plates. The exposure time ranged from twelve to sixty hours.

[1] R. C. Johnson and H. G. Jenkins, Proc. Roy. Soc. **A116**, 327 (1927).

[2] R. C. Johnson and N. R. Tawde, Phil. Mag. **13**, 501 (1932).

BANDS IN THE VISIBLE REGION

As Johnson and Tawde[2] pointed out, the bands in the visible region are unlike any in the spectra of N_2 and CO. The bands seem to be too diffuse to show much rotational structure.

In the writer's photographs, as in those of Johnson and Tawde, there is a background of many unresolved lines, extending from λ3500 into the red. These may be due to BO, but perhaps also to CO_2, since this has been observed to accompany the third positive CO bands,[3] which are very prominent in the present photographs. Table I contains measurements on the band heads by Johnson and Tawde, and by the present writer.

TABLE I. *Wavelengths of band heads observed by Johnson, Tawde and the present writer.*

Bands degrading to the violet				Bands degrading to the red			
Johnson and Tawde		Present work		Johnson and Tawde		Present work	
λ(A)	Int.	λ(A)	Int.	λ(A)	Int.	λ(A)	Int.
6399.7 ?	3	—	—	5476.3	2	—	—
6395.5 ?	1	—	—	5471.8	6	5470.8	6vd
6327.1 ?	3	—	—	5460.8	10	5460.1	4vd
6323.5 ?	2	—	—	5457.7	8	5456.8	8vd
6176.1	4	—	—	5451.1	4	4550.2	4vd
6112.2	4	—	—	5447.9	4	5447.0	4vd
				5441.5	1	—	—
5993.7	8	5993.8	8vd	5437.2	3	5436.7	3vd
5983.9	6	5984.4	6vd	5435.5	2	—	—
5975.6	4	5974.3	4vd	5421.6	2.	5420.6	2vd
				4465.0	8d	4464.9	8vd
—	–	5825.7	7vd	4461.7 ?	8d	4461.4 ?	6vd
5822.1	10	5822.1	10vd	4460.4 ?	6d	—	—
5814.3	8	5815.1	8vd	4443.5	8d	4443.5	6vd
5806.9	6	5807.3	6vd	4440.2 ?	6d	—	—
5803.5	6	5803.8	6vd	4438.8 ?	6d	—	—
5663.8	6	5664.0	6vd				
5655.9	3	—	—				
5649.8	1	—	—				
5646.3	1	—	—				

d = diffuse, vd = very diffuse.

[3] G. H. Dieke and J. W. Mauchly, Phys. Rev. **43**, 12 (1933).

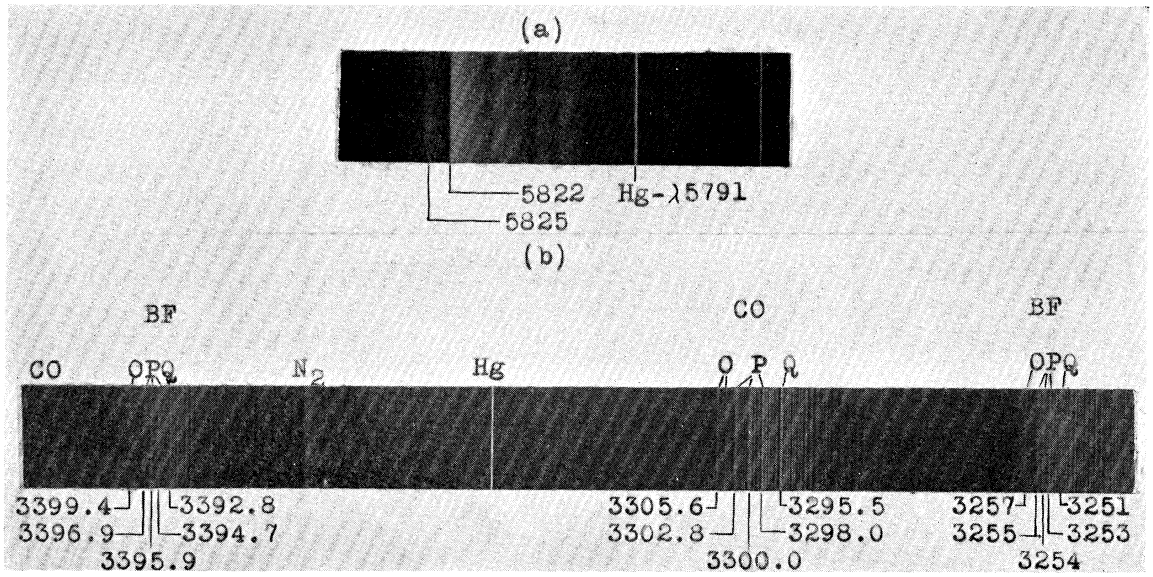

FIG. 1. (a) Part of visible spectrum, showing diffuse looking BF (?) bands. (b) Ultraviolet bands showing structure similar to the CO third positive band λ3305.

NEW BANDS

In addition to the bands listed above, the present investigation revealed three new bands, all in the ultraviolet region, and degrading to the ultraviolet. These bands differ greatly in appearance from those in the visible region. They appear to be similar in structure to those of the third positive group of CO (Fig. 1b, where one of the third positive CO bands appears strongly in the same region as the BF bands shown). Dieke and Mauchly[3] have made an analysis of these CO bands, and have shown them to belong to a $^3\Sigma \rightarrow {}^3\Pi$ transition. A comparison of the BF and CO bands seems to indicate that the former are either $^3\Sigma \rightarrow {}^3\Pi$ or $^3\Pi \rightarrow {}^3\Sigma$ transitions. The heads of the BF bands are lettered in Fig. 1b to correspond with similar heads of the CO bands. Proof that the *O*, *P* and *Q* branches have been identified correctly cannot be definitely established until an analysis of the bands has been made. The triplet separation shown by the new BF bands is much smaller than that in the $^3\Pi$ state of the third positive bands of the CO molecule, indicating that the BF bands are nearer case *b* type than the CO bands. The *O* branches of the BF bands are much fainter than the corresponding branches of the CO bands; in fact only one of the *O* branches is intense enough to be observed. This fact is further evidence that the $^3\Pi$ state of BF, presumably involved here, is nearer case *b* type than that of the third positive CO bands.

There are a number of faint lines on the long wavelength side of the observed *O* branches. These lines are hidden, in the case of the BF band λ3399.40, by the 5*B* band of CO at λ3419. Dieke and Mauchly[3] found similar lines on the long wavelength side of the *O* branches of the CO bands. They assigned these lines to an *N* branch (Table II).

TABLE II. *New bands.*

λ	Int.	λ	Int.	λ	Int.
3552.2	1	3399.40	3	3256.61	5
3549.9	2	3396.94	5	3254.76	7
3548.6	4	3395.96	6	3253.77	8
3547.3	4	3394.71	7	3252.73	9
3545.4 ?	4	3392.85	8	3250.94	10

There is evidence of another band in the region λ3720–λ3670, but the background is so strong that no definite proof of its existence can be offered.

Suggestions for Further Work

There are indications of the presence of faint bands in part of the region obscured by the background. It would be interesting to examine this region for such bands, and to determine whether they are to be classed with those observed in the ultraviolet, or with those in the visible region.

The rotational analysis of the ultraviolet bands should be feasible if undertaken with a stronger source and somewhat greater resolution than here. Such an analysis may be facilitated by the work of Dieke and Mauchly[3] on the probably similar third positive group of CO.

No explanation can be offered for the diffuse appearance of the bands in the visible region. It may be caused by predissociation in the upper state, or perhaps these bands are due to BF_2 or BF_3, and not to the diatomic molecule BF.

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Spectral and Impact Phenomena in the Faraday Dark Space

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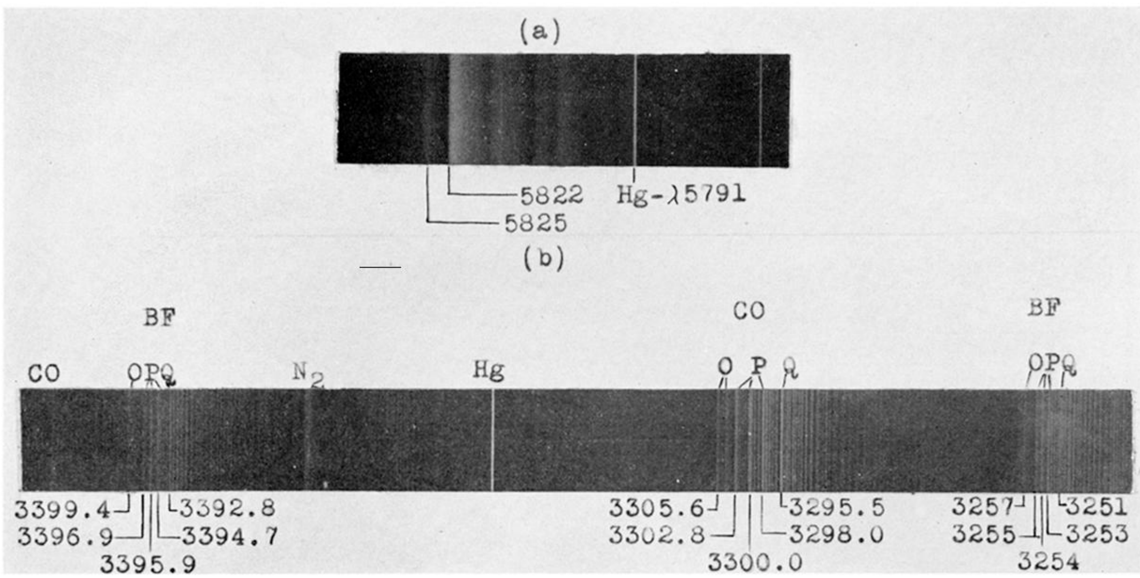
Observations on the spectra of the negative glow and Faraday dark space in pure helium and in helium containing a trace of nitrogen lead to the conclusion that in the negative glow the phenomena are due mainly to collisions of fast (primary) electrons with normal atoms while in the Faraday dark space impacts of the second kind between normal and metastable atoms are of primary importance. The metastable atoms present in the latter region are probably produced by the absorption of resonance radiation from the negative glow and are thus in the 2^1S state. The negative glow proper emits the He I and He II lines strongly and a band spectrum of He_2. The band spectrum is, relatively, much stronger in the region of transition between the negative glow and the Faraday dark space and this last region emits only the He I line $\lambda 5016$ (2^1S-3^1P) in sufficient intensity to be observed. When a trace of nitrogen is added to the helium, the N I spectrum replaces the He_2 bands in the transition region. A consideration of the phenomena observed leads to the conclusion that $He_2 2^{1,3}\Sigma$ molecules are formed by the union of a 1^1S atom and a $2^{1,3}S$ atom in a three body collision and that the possibility of observing the visible He_2 bands at all depends on the metastable nature of the $2^3\Sigma$ level of the He_2 molecule. These metastable molecules are excited to higher levels by slow electron impacts in pure helium, whereas when nitrogen is present, they are destroyed by impacts of the second kind with nitrogen molecules before they can be excited. N_2 molecules may be dissociated in these collisions, the dissociation occurring as a secondary consequence of the molecule's being raised to a higher electronic level from which dissociation occurs through predissociation or because the upper level is repulsive or simply because the molecule is excited to a degree above its dissociation asymptote. The effects from admixtures of oxygen and of carbon monoxide to helium and similar experiments on neon and argon support the conclusions drawn from the phenomena observed with helium and helium-nitrogen mixtures.

Introduction

The Faraday dark space is the name given to the feebly luminous space between the two regions of strong luminosity in the fully developed glow discharge. It is bounded fairly sharply at its anode end by the positive column and passes without sharp demarcation into the negative glow at its negative end. Early measurements on the electric field in this region indicated that the field is very small, or even reversed[1] for electrons, and more recent measurements[2] confirm this observation, the current being due to a concentration gradient[3] of ions and electrons. The properties of the negative glow and the Faraday dark space together approximate those

[1] J. J. Thomson, Phil. Mag. **18**, 441 (1909).
[2] McCurdy, Phil. Mag. **46**, 524 (1924); Compton, Turner and McCurdy, Phys. Rev. **24**, 597 (1924).
[3] Emeleus and Harris, Phil. Mag. **4**, 49 (1927).



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