

Ultra-Violet Band Systems of HF⁺ and DF⁺

ALTHOUGH band-systems of HCl⁺ and HBr⁺ have been known for many years, there is no definite spectroscopic information about HF⁺. Woods¹ observed a many-line spectrum in the ultra-violet region in discharges in the presence of hydrogen fluoride vapour, and what was apparently the same spectrum was later excited by Barrow and Caunt², who analysed five bands of a $v' = 0$ progression. They were unable to identify the emitter with certainty, and later experiments, carried out in the hope of finding suitable conditions for the excitation of the spectrum of the deuteride, were unsuccessful.

We have now found that the ultra-violet system may be excited reproducibly in hollow-cathode discharges, in the presence of a few millimetres pressure of helium, in which the hollow cathode contains potassium bifluoride. The corresponding system of the deuteride has also been observed in discharges with KDF₂ in the cathode.

The spectra consist of a large number of lines, without apparent regularity, in the region 2100–2650 Å. So far, we have assigned about 650 lines to nineteen bands in the hydride system and 300 lines to six bands in the deuteride system. Each band appears to consist of two branches, *P* and *R*. The earlier analysis of the hydride bands is confirmed, but the study of the isotope effect allows true vibrational quantum numbers to be assigned to the lower state.

The emitter of the bands is identified from the rotational and vibrational constants of the upper state, *B*. Agreement between the constants observed for the deuteride and those calculated from the hydride is obtained only if the ratio of reduced masses (ρ^2) has the value required for $\mu_{\text{HF}}/\mu_{\text{DF}}$ (= 0.52555). Values are given in Table 1.

Table 1. CONSTANTS FOR $B^2\Sigma^+$ OF DF⁺

	Observed	Calculated from hydride* (i)	(ii)
B_0	2.115	2.113	2.130 ₆
B_1	2.105	2.104	2.122
D_0	5.19×10^{-5}	5.22×10^{-5}	5.31×10^{-5}
D_1	5.48×10^{-5}	5.39×10^{-5}	5.49×10^{-5}
$\Delta G_{0,1}$	822.0	821.8	824.9

* (i) $\rho^2 = 0.52555 \frac{\mu(\text{HF})}{\mu(\text{DF})}$. (ii) $\rho^2 = 0.53000 = \frac{\mu(\text{OH})}{\mu(\text{OD})}$

Information about the lower state, *A*, cannot readily be summarized in equilibrium rotational and vibrational constants as anharmonic terms are large: moreover, we have information at present only on levels $v'' = 4$ to 10 in the hydride, and $v'' = 7$ to 10 in the deuteride. The extent of the departure from harmonic behaviour suggests that Dunham corrections may be important; however, a comparison of the constants so far determined shows that the simple isotope relations are at least approximately fulfilled (Table 2). A summary of the main constants for the two states of the hydride is given in Table 3.

The energy of dissociation of the lower state of the hydride may be obtained with some precision

Table 2. CONSTANTS FOR $A^2\Sigma^+$ OF DF⁺

	Observed	Calculated from hydride*
B_7	5.988	5.978
B_8	5.696	5.679
B_9	5.390	5.370
B_{10}	5.062 ₆	5.048
$\Delta G_{7,8}$	1,390.3	1,387.8
$\Delta G_{8,9}$	1,294.8	1,292.5
$\Delta G_{9,10}$	1,193.9	1,191.4

* With $\rho^2 = 0.52555$

Table 3. CONSTANTS FOR $A^2\Sigma^+$, $B^2\Sigma^+$ OF HF⁺

$A^2\Sigma^+$	$G_v = 2,977.6(v+\frac{1}{2}) - 111.91(v+\frac{1}{2})^2 + 4.317(v+\frac{1}{2})^3 - 0.2569(v+\frac{1}{2})^4$
	$B_v = 15.212 - 0.0746(v+\frac{1}{2}) - 0.00106(v+\frac{1}{2})^2 - 2.66 \times 10^{-7}(v+\frac{1}{2})^3$
	$r_e = 1.076 \text{ \AA.}$
$B^2\Sigma^+$	$v_0 = 57,258 \text{ cm.}^{-1}$
	$G_v = 1,153.4(v+\frac{1}{2}) - 17.2(v+\frac{1}{2})^2$
	$B_v = 4.027_7 - 0.0216(v+\frac{1}{2}) - 0.0011(v+\frac{1}{2})^2$
	$r_e = 2.092 \text{ \AA.}$

by a short extrapolation to $D' = 20,480 \text{ cm.}^{-1}$. A rough value for D'_0 may be obtained by linear extrapolation: this gives $D'_0 = 18,900 \text{ cm.}^{-1}$. With $v_{0,0} = 56,372 \text{ cm.}^{-1}$, we find that the separation of the atomic states at infinite internuclear distance is 54,800 cm.^{-1} . Since the extrapolation for the upper state amounts to about 15,000 cm.^{-1} , we cannot expect this estimate to be very precise, but it suffices for a plausible identification of the atomic products. The excited states of the neutral fluorine atom are crowded into a region lying within about 34,000 cm.^{-1} of the ionization limit, and neutral HF cannot then be the emitter. If, however, we examine the states giving rise to HF⁺, we find H(¹S₀) + F(²P) at 0 cm.^{-1} , H(²S_{1/2}) + F(³P) at 30,875 cm.^{-1} , H(²S_{1/2}) + F(¹D₂) at 51,748 cm.^{-1} and H(²S_{1/2}) + F(¹S₀) at 75,794 cm.^{-1} . It seems highly probable that state *A* correlates with H + F(²P), and *B* with H + F(¹D). Both atom pairs give $^2\Sigma^+$ states, and this fits in with the fact that the bands appear to possess only two branches: the spin-doubling has yet to be resolved. State *A* is then analogous to $A^2\Sigma^+$ in HCl⁺; state *B* to $A^2\Sigma^+$ in OH.

The ground-states of the molecules HCl⁺ and HBr⁺ are $^2\Pi_i$, correlating with H + X(²P): the analogous state in HF⁺ remains to be found. Whether it lies above or below $A^2\Sigma^+$ is not yet known; many unassigned lines in the ultra-violet region remain, and a search for bands of transitions $A^2\Sigma^+ - ^2\Pi_i$, $B^2\Sigma^+ - ^2\Pi_i$ is now in progress. Electron-impact studies might throw light on the question of which state is the ground-state. If $A^2\Sigma^+$ is the ground-state, then the ionization potential of HF is found to be 16.88 eV.; this may be compared with the estimate, 18.23 eV., given some years ago by Mulliken³.

J. W. C. JOHNS
R. F. BARROW

Physical Chemistry Laboratory,
University of Oxford.
Nov. 29.

¹ Woods, L. H., *Phys. Rev.*, **64**, 259 (1943).

² Barrow, R. F., and Caunt, A. D., *Proc. Phys. Soc.*, A, **67**, 68 (1954).

³ Mulliken, R. S., *Phys. Rev.*, **46**, 549 (1934).

Comparison of Threshold of Hearing for Bands of Noise and for Pure Tones

THE results of some measurements of the threshold of hearing for a pure tone and for a band of noise may be of general interest as they have a bearing on the resonance theory of hearing. (The connexion between such measurements and the resonance theory of hearing was pointed out by D. Boston at a meeting of the Physical Society of London in 1953.)

Comparisons were carried out on twenty-seven subjects by the free-field method in an anechoic room 24 ft. × 12 ft. × 9 ft. which contained only the subject, sitting on a chair facing the loud speaker 12 ft. away, and a microphone for measurement of the