

## The electronic spectra of HCl and HF<sup>1</sup>

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Received April 10, 1979

The absorption spectra of HCl and HF have been photographed at high dispersion in the vacuum ultraviolet region. In the HCl spectrum, many new band systems have been identified and 18 vibrational levels of the ionic  $B^1\Sigma$  state have been observed. The  $B^1\Sigma$  state is found to interact strongly with the Rydberg states. Although many bands have been analysed, much of the HCl spectrum remains unassigned. Analyses of bands associated with the lowest discrete  $^1\Pi$  and  $^3\Pi$  states of HF are presented together with the analyses of two  $^1\Pi-X^1\Sigma$  band systems which lie between the first and second ionization limit. The spectrum of HF is very complex and little of it has been analysed even though the spectral lines are sharp and well resolved. The theoretical problems in understanding the spectra of HCl and HF are discussed.

Les spectres d'absorption de HCl and HF ont été photographiés avec une grande dispersion, dans la région de l'ultraviolet sous vide. Dans le spectre de HCl, on a identifié plusieurs nouveaux systèmes de bandes et observé 18 niveaux vibrationnels de l'état ionique  $B^1\Sigma$ . On trouve qu'il y a interaction très forte entre l'état  $B^1\Sigma$  et les états de Rydberg. Bien qu'on ait analysé plusieurs bandes, un bon nombre des transitions du spectre de HCl restent à identifier. Les analyses des bandes associées aux plus bas états  $^1\Pi$  et  $^3\Pi$  de HF sont présentées en même temps que les analyses de deux systèmes de bandes  $^1\Pi-X^1\Sigma$  situés entre la première et la seconde limite d'ionisation. Le spectre de HF est très complexe, et une petite portion seulement de ce spectre a été analysée, bien que les raies soient fines et bien résolues. Les problèmes théoriques que pose l'interprétation des spectres de HCl et de HF sont discutés.

[Traduit par le journal]

Can. J. Phys., 57, 1650 (1979)

### 1. Introduction

The present work was undertaken as a study of the electronic spectrum of HF which had not been reported previously. When this spectrum was found to be extremely complex, a study of the absorption spectrum of HCl, which shows a great deal more regularity, was undertaken in the hope that it would be useful in interpreting the HF spectrum. As will be discussed more fully later, a considerable portion of the HCl spectrum and a small region of the HF spectrum have been analysed but a theoretical understanding of these spectra is almost completely lacking. The considerable volume of work which has been completed and the large effort needed to make further substantial progress in interpreting these spectra seem to warrant publication at this time.

The simplest picture of the excited electronic states of HF and HCl is one in which it is recognized that these molecules have a full shell of electrons and that all excited states must result from an increase of the principal quantum number of one of the electrons. Within this picture all excited states may be called Rydberg states and might be ex-

pected to have vibrational and rotational constants similar to those of the corresponding ion. There is of course much evidence from studies of other molecules that this picture has a very limited validity and that states with quite different characteristics might be found. In this paper only those states which have characteristics similar to those of the ion will be referred to as Rydberg states.

The rotational structures of the ground states of HCl and DCl are well known from numerous infrared and microwave studies (1). Absorption to the lowest excited electronic state, which is diffuse, has been studied by Romand (2). An emission band system of HCl in the 2000 Å region, which results from a transition between an ionic state, known as the  $V$  state, and the ground state, has been analysed by Jacques and Barrow (3). Their analysis has yielded the rotational and vibrational constants of the four lowest vibrational levels of the  $V$  state. High resolution absorption spectra of HCl and DCl for wavelengths down to 1200 Å have been measured and analysed by Tilford, Ginter, and Vanderslice (4) and by Tilford and Ginter (5). The present work consists largely of an extension of the high resolution absorption studies to shorter wavelength.

The ground state of HF is also well known from infrared and microwave studies (1) but prior to the

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present work little was known about the excited electronic states. The absorption to the lowest excited electronic state, which is diffuse, has been studied by Safary, Romand, and Vodar (6). An emission band system resulting from a  $V-X$  transition has been analysed by Johns and Barrow (7) and, as an earlier part of the present investigation, a more detailed report on the absorption and emission bands of this transition has been published by Di Lonardo and Douglas (8). In the present work the analysis of the absorption spectrum has been extended to give some further information on the electronic states of HF but much of this complex spectrum remains unanalysed.

## 2. Experimental

At wavelengths longer than 1200 Å the spectra of HCl and DCl have been rather completely analysed and no further work was carried out in this region of the spectrum. Using the Ar continuum with a 10.7 m concave grating spectrograph, we have photographed the absorption spectra of HCl and DCl between 1225 and 1075 Å at a dispersion of 0.24 Å/mm. Most of the spectra were photographed with the absorption cell at room temperature but for a few plates it was cooled to  $-120^{\circ}\text{C}$ . At wavelengths less than 1075 Å, spectra with a dispersion of 0.72 Å/mm were obtained.

The emission spectrum of HCl was photographed in the 1700–2375 Å region using the 10.7 m spectrograph. Compared with the earlier studies of this spectrum by Jacques and Barrow (3), the present spectrum extends further to the violet and is of considerably higher resolution.

The spectrum of HF was photographed at dispersions of 0.24 and 0.18 Å/mm. Further details are given in ref. 8.

## 3. HCl and DCl Results

### 3.1 Survey of Results

The spectra of HCl and DCl at wavelengths less than 1200 Å were found to contain thousands of sharp lines together with some lines broadened by predissociation and a few completely diffuse bands. In the long wavelength region of the spectrum, most of the sharp and slightly broadened lines can be grouped into bands and  $J''$  and  $\Delta J$  values can be assigned. However, starting from the  $83\,200\text{ cm}^{-1}$  region, there are a few clear lines which are unassigned and with increasing frequency the spectra grow more complex until, in the  $93\,000\text{ cm}^{-1}$  region, a large fraction of the lines are unassigned. At frequencies higher than  $93\,000\text{ cm}^{-1}$  only a few of the lines have been assigned.

Throughout this work the rotational constants of the ground state determined from the infrared spectra of HCl and DCl were accepted and the rotational levels of the upper state were determined from the calculated lower state levels and the assigned lines. For most bands, we have been able to determine  $\nu_0$ ,  $B_v$ , and  $D_v$  values for the upper states by fitting the levels to the expression

$$[1] \quad F(J) = \nu_0 + B_v J(J+1) - D_v J^2(J+1)^2$$

This expression was used even for states with  $\Omega > 0$ . For many of the bands the  $\Omega'$  value can be established by observing the first lines of the branches. Also from the isotopic rules and the separation of the  $\text{H}^{35}\text{Cl}$  from the corresponding  $\text{H}^{37}\text{Cl}$  band, the vibrational numbering of the excited state can usually be determined. The constants of the observed upper state levels of the  $B^1\Sigma$  state are given in Tables 2 and 3 and those of all other states in Tables 4 and 5.

### 3.2 The $B^1\Sigma$ State

Tilford and Ginter (5) have noted that the spectra of HCl and DCl show long progressions of  $^1\Sigma-X^1\Sigma$  bands which are associated with an ionic excited state. This ionic state, which is characterized by small vibrational intervals and rotational constants but a large dissociation energy, is of the type called a  $V$  state by Mulliken (9). To be consistent with accepted notation it will be denoted as the  $B^1\Sigma$  state. Jacques and Barrow (3) have observed the four lowest vibrational levels of this state in emission and have determined rotational and vibrational constants.

The wavenumbers of the absorption lines of the  $B^1\Sigma-X^1\Sigma$  bands are given in Table 1D.<sup>3</sup> In Table 2 we have listed the observed vibrational energy levels and rotational constants of the  $B^1\Sigma$  state of HCl and in Table 3 the corresponding information for DCl. For HCl, the numbering of the vibrational levels observed in absorption can be determined by a short extrapolation from the four lowest levels which have been observed in emission. Since for DCl the emission spectrum has not been measured and fewer bands are observed in absorption, the vibrational numbering cannot be determined with certainty. In Table 3 the levels have been given a relative vibrational numbering starting with  $N$  where  $N$  is probably  $12 \pm 1$ .

Although the vibrational numbering of the ob-

<sup>3</sup>All tables with numbers ending in D are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

TABLE 2. Constants of the  $B^1\Sigma$  state of HCl<sup>a</sup>

$\nu$	$H^{35}Cl$			$H^{37}Cl$		
	$T_0 + G(\nu)$	$B_\nu$	$10^4 D_\nu$	$T_0 + G(\nu)$	$B_\nu$	$10^4 D_\nu$
0	76 254.5	2.7397	1.12			
1	77 099.9	2.7649	1.37			
2	77 914.3	2.7917	1.55			
3	78 698.3	2.8320	2.01			
4	79 454.3	2.8739	2.34			
5	80 183.9	2.9213	2.75			
6	80 888.3	2.968	2.28	80 886.0		
7	81 569.8	3.046	4.1	81 567.1	3.039	3.8
8	82 225.9	3.156	6.6	82 222.9	3.151	6.9
9	82 839.8	3.682	43	82 837.0	3.651	39
10	83 434.1	4.808	-438	83 431.0	5.075	-220
11	84 207.7	4.301	-83	84 204.0	4.312	-78
12	84 746.9	4.012	3.6	84 742.4	4.010	4.0
13	85 277.6	4.270	-41	85 272.9	4.321	0.3
14	85 672.9	5.877	-20	85 669.8		
15	86 405.7	3.809	-84	86 400.1	3.817	-84
16	86 931.9	3.756	-9.6	86 925.8	3.755	-9.6
17	87 464.5	3.591	-13	87 458.5	3.564	-16
18	87 967.6	4.335	61	87 961.4	4.300	54
19	88 565.5	3.790	-36	88 558.8		
20	89 086.9	3.282	-16	89 080.3	3.310	-9.0
21	89 607.3	3.298	-25	89 599.8	3.265	-36
24	91 145.7	3.117	-75	91 137.8	3.110	-80
26	92 099.1	3.009	16	92 090.5		

<sup>a</sup>The constants of the  $\nu = 0, 1, 2$  and  $3$  levels have been taken from the work of Jacques and Barrow (3) but  $T_0 = 76\,254.5$  has been used. The constants of  $\nu = 4$  and  $5$  have been derived from our measurements of emission bands. All other constants are from the absorption bands.

TABLE 3. Constants determined from the absorption bands of the  $B^1\Sigma-X^1\Sigma$  system of DCl

$\nu'$	$D^{35}Cl$			$D^{37}Cl$		
	$T_0 + G(\nu')$	$B_{\nu}'$	$10^4 D_{\nu}'$	$T_0 + G(\nu')$	$B_{\nu}'$	$10^4 D_{\nu}'$
$N^a$	82 942.2	1.822	18	82 934.0	1.912	30
$N + 1$	83 389.4	2.198	111	83 382.7	2.195	110
$N + 2$	83 739.1	2.857	41	83 735.3	2.802	38
$N + 3$	84 298.2	2.166	-4.4	84 290.6	2.161	-5.5
$N + 4$	84 663.9	2.405	18	84 656.5	2.374	16
$N + 5$	84 952.3	3.252	34	84 946.4	3.215	32
$N + 6$	85 479.8	2.218	-46	85 470.4	2.295	-33
$N + 7$	85 842.8	2.143	-4.9	85 832.8	2.136	-6
$N + 8$	86 219.5	2.085	-59	86 208.8	2.081	-37
$N + 9$	86 587.2	2.275	11	86 576.6	2.261	10

<sup>a</sup> $N$  probability is  $12 \pm 1$ .

served absorption bands of HCl appears to be definite, there was a difference of  $55\text{ cm}^{-1}$  between the observed position of the 6-0 band and the position calculated from the constants given by Jacques and Barrow (3). An attempt was made to observe the 5-0 and 4-0 bands in absorption but the 5-0 band is covered by the very strong diffuse 1-0 band of the  $C-X$  system (4) and the 4-0 band, which must be very weak, is overlapped by the continuous absorption of HCl in the  $1250\text{ \AA}$  region. In order to investigate this problem further, we have extended

the analysis of the emission spectrum to include the 3-9, 4-9, and 5-9 bands and determined that  $\Delta G(3\frac{1}{2}) = 755.94$  and  $\Delta G(4\frac{1}{2}) = 729.62\text{ cm}^{-1}$  in the  $B$  state. With these new data the only low lying unobserved  $\Delta G$  interval of the  $B$  state is  $\Delta G(5\frac{1}{2})$  and we believe that the value of this interval can be determined to within less than  $1\text{ cm}^{-1}$  by interpolating between the lower and higher observed  $\Delta G$  values. With these new observed and calculated  $\Delta G$  values together with the band origin of the 6-0 band, the value of  $T_0$  of the  $B$  state was found to be  $76\,254.5 \pm$

TABLE 4. Constants determined from the absorption bands of HCl<sup>a</sup>

$\nu_0^b$	Intensity <sup>c</sup>	Assignment <sup>d</sup>	$\nu$	$B_\nu^e$	$D_\nu^e \times 10^3$
82 847.3 <sup>f</sup>	W	<i>F</i> 2	0	10.33( <i>PR</i> )	1.1
83 087.7	W	<i>G</i> 0 <sup>+</sup>	0	7.633	-5.5
83 780.2 } 83 778.1 }	M	<i>H</i> 0 <sup>+</sup>	0	6.6423	3.62
85 918.7 } 85 914.2 }	M	<i>H</i> 0 <sup>+</sup>	1	6.3305	-65
88 121.6	VW	<i>I</i> 1	0	9.836	0.70
88 684.5	VS	<i>J</i> 0 <sup>+</sup>	0	8.441	0.89
90 778.3	VS	<i>J</i> 0 <sup>+</sup>	1	7.908	-20.4
90 775.8					
88 968.1	W	<i>K</i> ?	0	10.4	6
88 971	W	<i>L</i> ?	0	?	?
89 282.0	S	<i>M</i> 0 <sup>+</sup>	0	9.654	-0.39
89 680.5	VS	<i>N</i> 1	0	9.423( <i>PR</i> ) 9.038( <i>Q</i> )	-0.78( <i>PR</i> ) -1.73( <i>Q</i> )
92 285.0 } 92 283.3 }	M	<i>N</i> 1	1	9.102( <i>PR</i> ) 8.793( <i>Q</i> )	-0.5( <i>PR</i> ) -2.4( <i>Q</i> )
89 912.3	W	<i>o</i> 2	0	10.575( <i>PR</i> ) 10.5( <i>Q</i> )	3.72( <i>PR</i> )
90 029.9	M	<i>o</i> 1	0	9.736( <i>PR</i> ) 9.676( <i>Q</i> )	-0.16( <i>PR</i> ) -1.44( <i>Q</i> )
90 133.4	M	<i>o</i> 0 <sup>±</sup>	0	10.62( <i>PR</i> ) 10.68( <i>Q</i> )	1.00( <i>PR</i> ) 2.41( <i>Q</i> )
90 653.8	VS	<i>P</i> 1	0	9.562( <i>PR</i> ) 9.973( <i>Q</i> )	16.4( <i>PR</i> ) 0.81( <i>Q</i> )
93 242.7 } 93 241.0 }	M	<i>P</i> 1	1	9.821( <i>PR</i> ) 9.590( <i>Q</i> )	-4.1( <i>PR</i> ) -0.2( <i>Q</i> )
91 491.6	M	<i>Q</i> 0 <sup>+</sup>	>0	5.788	-50
91 867.2	S	<i>R</i> 1	0	10.923( <i>PR</i> ) 10.4( <i>Q</i> )	12.7( <i>PR</i> )
92 328.3	W	<i>S</i> 2	0	9.217( <i>PR</i> ) 9.235( <i>Q</i> )	0.91( <i>PR</i> ) 2.4( <i>Q</i> )
92 446.8	S	<i>T</i> 1	0	10.049( <i>PR</i> ) 9.812( <i>Q</i> )	2.16( <i>PR</i> ) -0.28( <i>Q</i> )
92 998.3	S	<i>U</i> 0 <sup>+</sup>	>0	8.025	-1.9
92 934	M	<i>V</i>	1		
94 421.9 } 94 419.4 }	S	<i>W</i> 0 <sup>+</sup>	>0	8.66	-4

<sup>a</sup>All bands originate from the  $\nu = 0$  level of the ground electronic state.

<sup>b</sup>Where two values are given they refer to the H<sup>35</sup>Cl and H<sup>37</sup>Cl isotopic species.

<sup>c</sup>The intensities are rough estimates made from the photographs of the absorption bands using the notation very strong VS, strong S, medium M, weak W, very weak VW. On this scale the intensity of the strongest *B-X* bands is M and the *C-X* bands VS.

<sup>d</sup>Each state is designated by an arbitrarily chosen letter and by its  $\Omega$  value.

<sup>e</sup>*B* and *D* values are given for H<sup>35</sup>Cl only.

<sup>f</sup>The *B* and *D* values of this state are from ref. 5. The numbering of the lines of the *Q* branch is uncertain.

1 cm<sup>-1</sup>. Jacques and Barrow give  $T_0 = 76\,210$  cm<sup>-1</sup> but their value suffers from a large error arising from a long extrapolation of the lower state vibrational levels observed in infrared absorption up to those levels observed in emission. The new vibrational data could be used to revise the vibrational constants given by Jacques and Barrow but, as will be discussed in the following paragraphs, vibrational constants have little meaning for the *B* state.

A full report on the emission spectrum will be published at a later date.

The constants  $\nu_0$ ,  $B_\nu$ , and  $D_\nu$  of the *B* state which are given in Tables 2 and 3 were obtained by a least-squares fit of the observed levels to expression [1] even though the rotational lines of most of the bands with  $\nu' > 6$  suffer from local perturbations. Under these conditions the fit to the observed levels is poor and the constants depend on the

TABLE 5. Constants determined from the absorption bands of DCI<sup>a</sup>

$\nu_0^b$	Assignment <sup>c</sup>		$B_v^d$	$B_v^d$	$D_v^d \times 10^3$
82 909.5	<i>F</i>	2	0	5.164( <i>PR</i> ) 5.167( <i>Q</i> )	0.14( <i>PR</i> ) 0.18( <i>Q</i> )
83 944.9	<i>H</i>	0 <sup>+</sup>	0	3.296	-0.25
83 940.2					
85 131.8	<i>H</i>	0 <sup>+</sup>	1	3.855	18.7
85 125.8					
88 133.4	<i>I</i>	1	0	5.088( <i>PR</i> ) 5.092( <i>Q</i> )	0.121( <i>PR</i> ) 0.20( <i>Q</i> )
88 694.0	<i>J</i>	0 <sup>+</sup>	0	4.658	0.95
90 325.8	<i>J</i>	0 <sup>+</sup>	1	4.381	-1.57
90 323.5					
89 287.6	<i>M</i>	0 <sup>+</sup>	0	5.080	5.7
89 708.9	<i>N</i>	1	0	4.982( <i>PR</i> ) 4.879( <i>Q</i> )	0.08( <i>PR</i> ) -0.06( <i>Q</i> )
91 567.6	<i>N</i>	1	1	4.862( <i>PR</i> ) 4.779( <i>Q</i> )	0.17( <i>PR</i> ) 0.07( <i>Q</i> )
91 565.3					
89 956.8	<i>o</i>	2	0	5.267( <i>PR</i> ) 5.274( <i>Q</i> )	0.31( <i>PR</i> ) 0.32( <i>Q</i> )
90 057.6	<i>o</i>	1	0	5.062( <i>PR</i> ) 5.058( <i>Q</i> )	0.19( <i>PR</i> ) 0.20( <i>Q</i> )
90 167.8	<i>o</i>	0 <sup>±</sup>	0	5.281( <i>PR</i> ) 5.031( <i>Q</i> )	0.33( <i>PR</i> ) 3.05( <i>Q</i> )
92 015.4	<i>o</i>	1	1	5.165( <i>PR</i> ) 5.189( <i>Q</i> )	0.18( <i>PR</i> ) 0.33( <i>Q</i> )
92 013.1					
91 890.6	<i>P</i>	1	0	5.395( <i>PR</i> ) ~5.4( <i>Q</i> )	3.57( <i>PR</i> )
88 988.4	<i>X</i>	2	0	4.947( <i>PR</i> ) 4.955( <i>Q</i> )	2.0( <i>PR</i> ) -0.7( <i>Q</i> )
89 006	<i>X'</i>	1	0	~5.1	

<sup>a</sup>All bands originate from the  $\nu = 0$  level of the ground electronic state.

<sup>b</sup>Where two values are given they refer to the  $H^{35}Cl$  and  $H^{37}Cl$  isotopic species.

<sup>c</sup>The intensities are rough estimates made from the photographs of the absorption bands using the notation very strong VS, strong S, medium M, weak W, very weak VW. On this scale the intensity of the strongest *B-X* bands is M and the *C-X* bands VS.

<sup>d</sup>Each state is designated by an arbitrarily chosen letter and by its  $\Omega$  values.

number of levels observed. The constants given in the tables therefore must be accepted with great caution. In spite of the difficulties, the  $\nu_0$  and  $B$  values do give a useful description of the vibrational and rotational levels of the  $B$  state.

Tables 2 and 3 show that the vibrational spacing and the rotational constants of the  $B^1\Sigma$  levels are highly irregular. As will be discussed more fully in Sect. 3.5, there are additional bands which could be considered to belong to the  $B-X$  system but which have been omitted since their inclusion would make the vibrational progression even more irregular. In Fig. 1 we have plotted the deviation of the wavenumbers of the  $B^1\Sigma$  levels of HCl from those given by a simple expression used to represent the levels. Since this expression is not unique the deviations plotted in Fig. 1 serve only as a means of visualizing the severe perturbation in the positions of the vibrational levels. The behaviour of the DCI levels is rather similar. The peculiarities of the  $B$

and  $D$  values parallel those of the vibrational levels and indicate that the  $B^1\Sigma$  state is strongly mixed with one or more states which have higher  $B$  values.

### 3.3 $F^1\Delta$ State

Tilford and Ginter (5) have identified a  $^3\Delta$  state in the  $82\,000\text{ cm}^{-1}$  region and from the positions of the  $^3\Delta_2$  component relative to the  $^3\Delta_1$  and  $^3\Delta_3$  components it can be predicted that the corresponding  $^1\Delta$  state should lie near  $82\,900\text{ cm}^{-1}$ . In this region they found a 0-0 band of HCl with a somewhat overlapped  $Q$  branch and an  $R$  branch which could be followed down to  $R(0)$ . The  $P$  branch of the band was overlapped by a strong diffuse band. Based on the existence of an  $R(0)$  line and a  $Q$  branch they concluded that the excited state had an  $\Omega$  value of one and tentatively assigned it as the  $g^3\Sigma^-(1)$  state. We also have observed this band and have confirmed the existence of a line at

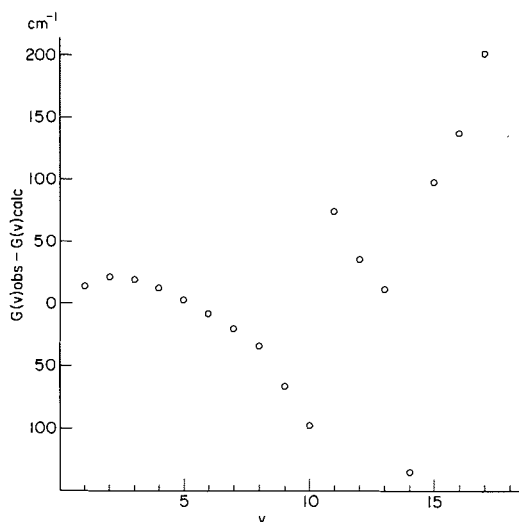


FIG. 1. The differences between the observed and calculated energies of the vibrational levels of HCl in the  $B^1\Sigma$  state. The energies are calculated from the expression  $G(v) = 842.7v - 11.5v^2$ .

the expected position of the  $R(0)$  line. However, on our spectra of HCl at  $-120^\circ\text{C}$ , whereas the  $R(1)$  line becomes stronger compared with the spectra of room temperature HCl, the  $R(0)$  line disappears completely. We therefore have concluded that the apparent  $R(0)$  line is in fact a stray high  $J$  line and the  $R$  branch ends at  $R(1)$ . The upper state is therefore an  $\Omega = 2$  state and fits very well as the  $F^1\Delta$  state predicted by Tilford and Ginter. The assignments of the closely packed lines of the  $Q$  branch are uncertain. In DCl the corresponding band is at  $82909.5\text{ cm}^{-1}$ . The wavenumbers of the lines of the  $F^1\Delta$  bands of HCl and DCl are given in Table 6D.

### 3.4 $G0^+$ State

The spectrum of HCl shows a weak but very clear band consisting of a  $P$  and an  $R$  branch with its band origin at  $83087.7\text{ cm}^{-1}$ . Since the lines of the band show no  $\text{H}^{35}\text{Cl}$ ,  $\text{H}^{37}\text{Cl}$  isotope splitting it must be a  $0-0$  band. The wavenumbers of the lines are given in Table 7D. The rotational levels of the upper state are somewhat irregular and the differences between the wavenumbers of the observed lines and those calculated from the constants in Table 4 are as high as  $0.6\text{ cm}^{-1}$ . The  $R$  branch can be followed only to  $R(5)$  although there are two overly strong unassigned lines which could be the perturbed  $R(6)$  and  $R(7)$  lines. The lines of the  $P$  branch beyond  $P(7)$  are overlapped by the strong diffuse  $2-0$  band of the  $C^1\Pi-X^1\Sigma$  system. The corresponding band of DCl has not been found, probably because it lies under the strong  $3-0$  band of the  $C^1\Pi-X^1\Sigma$  system (4).

### 3.5 $H0^+$ State

There are two bands in the spectrum of HCl which are assigned to the  $H0^+-X^1\Sigma$  system. This assignment is by no means obvious since the vibrational levels of the excited state have rather unusual characteristics. The wavenumbers of the lines of the  $H-X$  system are given in Table 8D. It is useful at this stage to state our conclusion that the  $H0^+$  state has its origin in a Rydberg state but that it is so strongly mixed with  $B^1\Sigma$  that in most respects it resembles the  $B$  state.

The longer wavelength band of the two lies at  $83780.2\text{ cm}^{-1}$ . The  $B$  value of the excited state is  $6.64\text{ cm}^{-1}$  which is much lower than that of the ground state of  $\text{HCl}^+$ . The  $\text{H}^{35}\text{Cl}$ ,  $\text{H}^{37}\text{Cl}$  isotope shift is  $2.1\text{ cm}^{-1}$  which normally would indicate that the upper state vibrational quantum number must be greater than zero but no vibrational level of this state can be found at longer wavelengths. The possibility that the upper state level is a member of the  $B^1\Sigma$  progression was considered but if this level is inserted in the progression, the vibrational spacing becomes more irregular. Also the isotope shift is somewhat less than that of the vibrational levels of the  $B$  state in this region and the  $B$  value of this band is higher than those of the  $B$  state. We have therefore chosen to assign this level to a separate electronic state which we have denoted as the  $H$  state.

The second of the two levels, which lies at  $85918.7\text{ cm}^{-1}$ , has a similar small  $B$  value and large isotope shift. The rotational structure of this level is perturbed and rotational constants have little meaning. The lowest few rotational levels indicate a  $B$  value of about  $7\text{ cm}^{-1}$  but the highest observed levels indicate a much higher value. Even though the assignment results in a value of only  $2138.5\text{ cm}^{-1}$  for  $\Delta G(\frac{1}{2})$ , we have assigned this vibrational level as the  $v = 1$  level of the  $H0^+$  state.

The two corresponding states of DCl are found at  $83944.9$  and  $85131.8\text{ cm}^{-1}$ . The  $v = 0$  band is clear but the  $v = 1$  band is overlapped and only for the  $D^{35}\text{Cl}$  species are the lines strong enough to allow an evaluation of the constants. From the few  $D^{37}\text{Cl}$  lines which can be seen in the  $v = 1$  band an isotopic shift of  $\sim 4.6\text{ cm}^{-1}$  can be determined.

The  $H$  state and its interaction with the  $B$  state will be discussed more fully in Sect. 4.

### 3.6 $I1$ State

To shorter wavelengths from the  $H^1\Sigma$ ,  $v = 1$  band there is a long region containing only bands of the  $B^1\Sigma$  system and some weak unidentified lines. At  $88121.6\text{ cm}^{-1}$  a rather weak band with regular  $P$ ,  $Q$ , and  $R$  branches is observed in the HCl spectrum. The structure of the band and the lack of resolved

isotopic structure indicate that the upper state is a  $\Omega = 1, v = 0$  state. The corresponding band of DCI has been observed. The wavenumbers of the lines of the  $I-X$  system are given in Table 9D.

### 3.7 $J0^+$ State

At  $88\,684.5\text{ cm}^{-1}$  the HCl spectrum shows a very strong band which has only a  $P$  and an  $R$  branch. The rotational structure is somewhat perturbed with the perturbation reaching its maximum at  $J' = 9$  but the analysis is simple and unambiguous. Since no chlorine isotopic splitting is observed in the lines, it must be a  $0-0$  band. At  $90\,778\text{ cm}^{-1}$  there is a similar band which shows an isotopic splitting and which we have assigned as the  $1-0$  band. Although the  $B$  values of the upper states and their isotopic effects qualitatively seem to indicate that the two bands belong to the same system, there are difficulties in this assignment. The vibrational spacing in the  $J$  state with this assignment is only  $2094\text{ cm}^{-1}$  and the isotopic splitting is greater than that expected for this vibrational frequency.

The two corresponding bands of DCI are at  $88\,694.0$  and  $90\,325.8\text{ cm}^{-1}$ . The strength of these bands, their  $B$  values and their position in the spectrum make this assignment rather secure. However, neither the rotational constants nor the vibrational spacing agree well with the values calculated from the HCl spectrum by the isotope rules. It appears probable that the  $J$  state is interacting strongly with some other state (possibly the  $B$  state). The wavenumbers of the lines of the  $J-X$  system are given in Table 10D.

### 3.8 $K$ and $L$ States

In a complex region of the spectrum near  $89\,000\text{ cm}^{-1}$  two bands which show no isotopic splitting have been observed. The first of these bands, denoted as the  $K-X$  band, has a  $P$  and an  $R$  branch which can be represented by reasonable  $B'$  and  $D'$  values. It is possible that a number of strong unassigned lines in the region where the  $Q$  branch should occur may be lines of a perturbed  $Q$  branch. The second band, denoted as the  $L-X$  band, also has clear  $P$  and  $R$  branches but the levels of the upper state cannot be fitted by [1]. A reasonable fit of the levels of the  $L$  state can be obtained by assuming that they are the  $F_3$  levels of a  $^3\Sigma^-$  state which can be represented roughly by  $BN(N+1)$  where  $N = J + 1$  but there is no other evidence to confirm this assignment. The wavenumbers of the lines of the  $K-X$  and  $L-X$  bands are given in Tables 11D and 12D, respectively.

### 3.9 $M0^+$ State

At  $89\,282.0\text{ cm}^{-1}$  there is a HCl band with only  $P$  and  $R$  branches of medium strength. The chlorine

isotope effect is not resolved. Up to  $R(4)$  and  $P(6)$  the lines of the branches are clear and strong but beyond these points no lines can be found. It appears that levels of the upper state with  $J \geq 5$  are either strongly perturbed or predissociated.

The corresponding band of DCI lies at  $89\,287.6\text{ cm}^{-1}$ . The rotational levels of the upper state are perturbed at  $J' = 3$  and  $4$  and this perturbation causes extra lines to appear in the band. The perturbation in the  $J' = 4$  level is most unusual in that two extra  $R(3)$  and  $P(5)$  lines appear in the spectrum.

The wavenumbers of the lines of the  $M-X$  system are given in Table 13D.

### 3.10 $N1$ State

At  $89\,680.5\text{ cm}^{-1}$  there is a strong regular band of HCl with  $P$ ,  $Q$ , and  $R$  branches and no chlorine isotope shift. A weaker band of the same type at  $92\,285.0\text{ cm}^{-1}$  which shows a chlorine isotope shift of  $1.7\text{ cm}^{-1}$  has been assigned as the  $1-0$  band of the same electronic transition. In DCI the corresponding bands are at  $89\,708.9$  and  $91\,567.6\text{ cm}^{-1}$ . These bands also are free of local perturbations. The hydrogen and chlorine isotope shifts of the  $N$  state follow the isotopic rules rather well and the constants of the states are close to those of the ground states of the  $\text{HCl}^+$  and  $\text{DCI}^+$  ions. Thus it appears that the  $N$  state is a Rydberg state which suffers from little or no interactions with other states.

The wavenumbers of the lines of the  $N-X$  bands are given in Table 14D.

### 3.11 $o^3\Pi$ State

Three bands lying near  $90\,000\text{ cm}^{-1}$  have been assigned as the three components of the  $0-0$  band of a  $^3\Pi-X^1\Sigma$  transition. The three bands, which are roughly equally spaced, have  $P$ ,  $Q$ , and  $R$  branches. There seem little doubt that the  $\Omega$  value for the  $89\,912.29$  band is 2 but for the other two bands all that can be stated with certainty is that  $\Omega = 0$  or 1. The  $\Lambda$  doubling of the state assigned as  $^3\Pi_2$  is small whereas that of the other two components is appreciable. The relative effective  $B$  values of the three components of the upper state do not follow the simple rules expected for a  $^3\Pi$  state (10). The evidence to support the assignment of the three bands as the three components of a  $^3\Pi-X^1\Sigma$  transition is limited and the assignment must be regarded as tentative. In the spectrum of DCI the three corresponding bands are observed. The wavenumbers of the lines of the  $o-X$  system are given in Table 15D.

### 3.12 $P1$ State

One of the strongest bands in the HCl spectrum is a band with  $P$ ,  $Q$ , and  $R$  branches at  $90\,653.8\text{ cm}^{-1}$ . In spite of the strength of the low  $J$  lines of the band

the high  $J$  lines are weak. It appears likely that there are interactions between the upper state of this band and the  $v = 1$  level of the  $J$  state and also possibly the  $v = 24$  level of the  $B^1\Sigma$  state but these interactions have not been analysed. A similar band lying at  $93\,242.7\text{ cm}^{-1}$  which shows an isotope shift has been assigned as the 1-0 band of the system. In the DCl spectrum, the corresponding 0-0 band has been observed but the region where the 1-0 band is expected has not been measured. The wavenumbers of the lines of the  $P-X$  bands are given in Table 16D.

### 3.13 Other Bands

At wavelengths shorter than that of the  $P-X$  band, seven other bands of HCl have been found. The constants which have been derived from these bands are given in Table 4 and the wavenumbers of the lines are given in Table 17D. These bands do not give a good description of the spectrum in the  $91\,000$  to  $94\,000\text{ cm}^{-1}$  region since there are many unassigned lines. The DCl spectrum has not been analysed in this region. There are, however, two bands of DCl near  $89\,000\text{ cm}^{-1}$ , which have been designated as the  $X$  and  $X'$  bands, for which the analogous HCl bands have not been found. The wavenumbers of the lines of these bands are given in Table 18D.

### 3.14 The Short Wavelength Region

In the region between  $1063$  and  $1070\text{ \AA}$  the argon source gives no continuum and we have not observed the spectra of HCl and DCl. From  $1053\text{ \AA}$  to the ionization limit the spectra have been photographed in the first order of the grating using the He continuum. No attempt was made to carry out rotational analyses of bands photographed at this low dispersion. The spectrum in this region does show many discrete bands up to and even beyond the ionization limit. A few of these bands could be analysed from the first order spectra but most of them appear to be perturbed and complex.

No obvious Rydberg series are seen in the spectrum. Near the ionization limit at  $972\text{ \AA}$  the spectrum is complex with no strong sharp features. At somewhat longer wavelengths, between  $980$  and  $1050\text{ \AA}$ , two series of strong features, which are more evident in the spectrum of DCl than HCl, can be fitted roughly by the two expressions

$$\nu_n = \left( \frac{103490}{102840} \right) - \frac{109737}{(n - 0.2)^2}$$

In these expressions  $102840$  and  $103490$  correspond to the two ionization limits of HCl as determined by photoelectron spectroscopy (1). Seven members of these series can be seen but the lower members are broad features obviously consisting of several

bands. The lowest members of the calculated series at  $89\,492$  and  $88\,842\text{ cm}^{-1}$  do not correspond closely to any strong bands. The lowest members of Rydberg series can seldom be represented by a simple formula and it is possible that the two strong bands at  $90\,653$  and  $89\,680\text{ cm}^{-1}$  are the two lowest members of these series. At this time it is still uncertain whether or not a Rydberg series has been observed.

## 4. Discussion, HCl

Although there are many difficulties in understanding of the HCl spectrum, it is of some value to discuss the problem from the simplest point of view. All excited states of HCl must be Rydberg states in that, at the bond distance of the ground state, they result from the excitation of an electron to some empty level with a higher principal quantum number. The simplest representation of a Rydberg state is one which assumes that it results from a single electron configuration consisting of the molecular ion core together with an electron in a Rydberg orbital which can be specified by the three quantum numbers  $n$ ,  $l$ , and  $\lambda$ . For HCl the core has a  $^2\Pi$  ground state and a  $^2\Sigma$  state which lies  $28\,628\text{ cm}^{-1}$  higher in energy (11). Thus vertical excitation of HCl should lead to states resulting from configurations  $(^2\Pi)(n\lambda)$  and, at somewhat higher energy, states resulting from the configurations  $(^2\Sigma)(n\lambda)$ .

If, from this simple point of view, we attempt to assign the observed excited states of HCl, then the lowest states, which give the continuum in the  $1550\text{ \AA}$  region, can be assigned as the  $^1\Pi$  and  $^3\Pi$  states resulting from the  $(^2\Pi)(4s\sigma)$  configuration. The discrete  $^1\Pi$  and  $^3\Pi$  states reported by Tilford *et al.* (4) must result from the  $(^2\Pi)(4p\sigma)$  configuration. It is interesting to note that the vibrational constants of these states are rather similar to (but slightly larger than) those of the ground state of the ion and that, if the interaction between the singlet state and the three components of the triplet state are taken into account (12), the  $B$  value is almost identical with that of the ground state of the ion. It has been noted by previous authors that the  $B^1\Sigma$  state must result from the  $(^2\Sigma)(4s\sigma)$  configuration. Although the lowest vibrational level of the  $B^1\Sigma$  state lies at  $76\,254\text{ cm}^{-1}$ , at the bond distance of the ground state it is  $\sim 20\,000\text{ cm}^{-1}$  higher and thus, as expected, well above the  $^1\Pi$  state resulting from the  $(^2\Pi)(4s\sigma)$  configuration.

The next higher electron configuration above  $(^2\Pi)(4p\sigma)$  probably is  $(^2\Pi)(4p\pi)$  which gives  $^1\Sigma^+$ ,  $^1\Sigma^-$ ,  $^1\Delta$ ,  $^3\Sigma^+$ ,  $^3\Sigma^-$ , and  $^3\Delta$  states. In this region Tilford and Ginter (5) have found  $^3\Pi$ ,  $^1\Pi$ ,  $^3\Delta$ , and  $^3\Sigma^-(1)$  states (as noted in Sect. 3.3 the  $^3\Sigma^-(1)$  state has been reassigned as  $^1\Delta$ ). The positions of these



observed bands indicate one of the difficulties in attempting to assign states since the  $^3\Pi$  and  $^1\Pi$  states which result from a  $(^2\Pi)(5s\sigma)$  or  $(^2\Pi)(3d\sigma)$  configuration must lie within the energy range spanned by the states arising from the  $(^2\Pi)(4p\pi)$  configuration.

It seems likely that the  $H$  state which gives the strong band at  $83\,780\text{ cm}^{-1}$  is the  $^1\Sigma^+$  state arising from the  $(^2\Pi)(4p\pi)$  configuration. Unlike the lower  $^1\Pi$  and  $^3\Pi$  states, the  $B$  and  $\Delta G(\frac{1}{2})$  values of the  $H^1\Sigma$  state are much lower than those of the ground state of the ion and the lowest observed level, which we have assigned as the  $v = 0$  level, shows a substantial chlorine isotope shift. Qualitatively these unexpected characteristics can be accounted for by assuming that there is a strong interaction between the  $H$  and the  $B$  states. This mixing causes the  $B_v$  values of the vibrational levels of the  $B^1\Sigma$  state to rise as the levels approach the lowest vibrational level of the  $H$  state and this pattern tends to repeat at the  $v = 1$  level of the  $H$  state. At the same time the mixing causes a sharp reduction in the  $B$  value of the  $H$  state and the transfer of some of the large isotope effect of the  $B$  state to the  $H$  state.

An attempt was made to treat the mixing of the  $B$  and  $H$  states more quantitatively but with little success. Probably one reason for the failure is the presence of other interacting states. For example, there is a weak band at  $83\,087\text{ cm}^{-1}$  which has an upper state  $B$  value of only  $7.6\text{ cm}^{-1}$ . This state possibly could be the  $0^+$  component of the expected  $^3\Sigma^-$  state. Also, in the region of the  $H-X$  bands there are a number of weak unidentified lines which seem to indicate the presence of additional perturbed states.

At higher energies no reliable correlations have been made between the observed states and electron configurations since there seems to be no basis for making the assignments. We have, for example, attempted to assign the  $J$ ,  $M$ , and  $I$  states as the  $^1\Sigma^+$ ,  $^3\Sigma^-(0^+)$ , and  $^1\Delta$  states arising from the  $(^2\Pi) 3d\pi$  configuration since they lie in the order predicted by Greening (13) and are at the expected energy for such states. The  $B$  value of the  $J$  state is, however, quite different from those of the  $M$  and  $I$  states and of the ground state of the ion thus suggesting a substantial mixing of configurations and it is difficult to predict the effect of this mixing on the ordering of states. As noted above, there is experimental evidence elsewhere that states from different configurations overlap in energy and that states from different configurations, such as the  $B$  and  $H$  states, interact strongly. Also the many local rotational perturbations which have been observed give evidence of other interactions and it is likely that

many of the unassigned lines result from states in which the perturbations have become so great that it is difficult to recognize the band structure. A lack of theoretical guidance has hampered the analysis of the spectrum. Some of the interactions between the Russel-Saunders states, such as  $l$  uncoupling and the changes in spin coupling as the energies of the state approach the ionization potential, are understood in principle even though the large matrices necessary to deal with the problem have not been calculated. The understanding of other interactions such as the mixing of several configurations would require a very detailed *ab initio* calculation of the states. While a calculation of sufficient accuracy to give a positive identification of all the observed bands is probably impossible, even a less exact treatment would be useful in assigning some of the more prominent features.

## 5. HF Results

The absorption spectrum of HF was photographed at high resolution in the  $660\text{--}1100\text{ \AA}$  range. Aside from the bands of the  $B-X$  system reported earlier (8) and the few bands discussed in the following sections, the spectrum consists of many sharp well-resolved lines showing no obvious band structure. In this respect the spectrum of HF is more complex than that of HCl. In the following sections the few bands which have been analysed are described. All the absorption bands originate from the  $v = 0$  level of the electronic ground state and since the constants of this state are well known (1), we have determined only upper state constants.

### 5.1 $b^3\Pi$ State

The absorption spectrum of HF is similar to that of HCl in that the lowest discrete state which can be observed is a  $^3\Pi$  state. Rather few lines are observed in the weak  $0-0$  band and even less in the  $1-0$  band. The position of the  $^3\Pi_1$  component with respect to the  $^3\Pi_0$  and  $^3\Pi_2$  components shows that it interacts strongly with the nearby  $C^1\Pi$  state. The perturbations of the  $B^1\Sigma$  bands in the region of the  $^3\Pi$  state indicate that there are significant  $b^3\Pi-B^1\Sigma$  interactions. Also the large  $\Lambda$  doubling, particularly in the  $^3\Pi_0$  component, indicates a strong  $\Pi-\Sigma$  interaction. No satisfactory fit to the rotational levels was obtained with any of the simple closed expressions representing the levels of a  $^3\Pi$  state. It appears that a satisfactory treatment of the  $^3\Pi$  state would require an evaluation of its interaction with the  $C^1\Pi$  and  $B^1\Sigma$  states and probably with at least one other  $\Sigma$  state. Since the number of observed lines is small and several of these are overlapped, we have not attempted such a treat-

ment. We have found that the constants  $v_0 = 104\,348$ ,  $B_0 = 15.8$ ,  $A = -144$ , and Kovacs'  ${}^1\Pi-{}^3\Pi$  interaction constant  $\beta = -32\text{ cm}^{-1}$  give a very rough fit to the upper levels of the 0-0 band. For the 1-0 band even less lines were identified with certainty and no constants were determined except  $\Delta G(\frac{1}{2}) \approx 2679\text{ cm}^{-1}$ . The wavenumbers of the lines of this band system are given in Table 19D.

### 5.2 $C\ {}^1\Pi$ State

In the HF spectrum a progression of  ${}^1\Pi-X\ {}^1\Sigma$  bands is readily identified and the corresponding progression is observed in the spectrum of DF. These bands appear to be the analogs of the  $C\ {}^1\Pi-X\ {}^1\Sigma$  bands of HCl but they are much less diffuse. The wavenumbers of the lines of the  $C\ {}^1\Pi-X\ {}^1\Sigma$  bands are given in Table 20D.

The  $P$  and  $R$  branches of all the bands are irregular and the lines cannot be fitted by any simple expression. The lines of the  $Q$  branches do not suffer from similar perturbations and form quite regular series. It seems likely that the perturbations of the upper levels of the  $P$  and  $R$  branch lines arise from interactions between the  ${}^1\Pi$  and the  $B\ {}^1\Sigma$  state but the symmetry of the levels forbids a similar interaction with the upper levels of the  $Q$  branch. The constants of the upper state, which are given in Table 21, were determined from the lines of the  $Q$  branches.

### 5.3 $D\ {}^1\Sigma$ State

In the region of  $112\,000\text{ cm}^{-1}$  there is a clear but perturbed  ${}^1\Sigma-X\ {}^1\Sigma$  band. The wavenumbers of the lines of this band are given in Table 22D. The perturbations in the levels of the upper state prevent the determination of accurate constants but rough values of  $v_0$  and  $B_0$  are  $112\,175$  and  $14.4\text{ cm}^{-1}$ . It is interesting to note that there appear to be two additional  $P(4)$  and  $R(2)$  lines in the band.

### 5.4 $Y\ {}^1\Pi$ and $Z\ {}^1\Pi$ Bands

At wavelengths less than that of the first ionization limit, two similar band systems showing well-

resolved rotational structure were observed. The bands appear relatively weakly on our plates since the path length of HF which we could use was limited by the continuous absorption. The vibrational structure of these two band systems was observed by photoionization mass spectrometry (14), and later studies by the same method showed the rotational structure.<sup>4</sup> The wavenumbers of the lines of these bands are given in Table 23.

The first two or three lines of the  $Q$  branch are sharp and easily measured but the lines of higher  $J$  values are diffuse and difficult to observe. The lines of the  $P$  and  $R$  branches are somewhat weaker, as expected for a  ${}^1\Pi-{}^1\Sigma$  transition and, since they also become more diffuse with increasing  $J$ , very few lines of these branches are measurable. The bands are free from perturbations and, in spite of the small number of clear lines, the analysis presents no difficulty. The limited number of clear lines does, however, severely limit the accuracy of the upper state constants derived from the bands. The band origins and the  $B$  values derived from the  $Q$  branches are given in Table 24.

## 6. HF Discussion

The  $b\ {}^3\Pi$  and  $C\ {}^1\Pi$  states need little comment. These states are similar to the lowest discrete Rydberg states observed in HCl and the other halogen hydrides. The vibrational and rotational constants of these states are similar to those of the ground state of  $\text{HF}^+$  thus indicating that they probably arise from a relatively pure ( ${}^2\Pi$  core)  $3p\sigma$  configuration.

The only bands we have analysed between the region of the  $C\ {}^1\Pi$  state and the ionization limit are the bands of the  $B\ {}^1\Sigma$  state and the single band of the  $D\ {}^1\Sigma$  state. No assignments have been made for the hundreds of well-resolved lines which are observed. Some of the difficulties in the analysis probably arise from a large number of local perturbations. The many perturbations in the lines of the  $B\ {}^1\Sigma-X\ {}^1\Sigma$  bands must be associated with corresponding perturbations in the Rydberg states. Since the  $\omega$  and  $B$  values of the Rydberg and the  $B$  states differ greatly, most of these perturbations will appear as random displacements of lines rather than as systematic displacements of bands or portions of branches. Although such perturbations will increase the difficulty in analysing the spectrum, they alone would not prevent the assignment of many of the lines. It is probable that the several difficulties arising from coupling conditions and from interactions between Rydberg states, which

TABLE 21. Constants of the  $C\ {}^1\Pi$  states of HF and DF determined from the  $Q$  branches of the  $C\ {}^1\Pi-X\ {}^1\Sigma$  bands

Molecule	Vibrational level	$T_0 + G(v)$	$B_v$	$D_v \times 10^3$
HF	0	105 091.0	16.033	-0.7
HF	1	107 727.4	15.473	0.9
HF	2	110 256.2	15.009	1.8
HF	3	112 662.1	14.61	
DF	0	105 238.3	8.582	0.7
DF	1	107 199.0	8.416	0.6
DF	2	109 100.6	8.322	0.4

<sup>4</sup>W. A. Chupka. Private communication.

TABLE 23. Wavenumbers of the lines of the  $Y^1\Pi-X^1\Sigma$  and  $Z^1\Pi-X^1\Sigma$  bands of HF

$J$	0-0 band $Q(J)$	1-0 band $Q(J)$	2-0 band $Q(J)$	3-0 band $Q(J)$	4-0 band $Q(J)$
$Y^1\Pi-X^1\Sigma$ bands					
1	141 651.5	142 944.1	144 019.3	144 836.7	145 396
2	609.0	899.1	969.9	782.0	
3		830.8	895.4	700.3	
4			797.0	590.2	
$Z^1\Pi-X^1\Sigma$ bands					
1	147 191.4	148 495.7	149 565.0	150 368.2	
2	142.9	444.8	511.7	309.5	
3		370.7	431.0	221.0	
4			328.0	104.9	

NOTE:  $R(0)$  lines of the 2-0 and 3-0 bands of the  $Y-X$  system are at 144 066.8 and 144 881.1 and the  $R(0)$  line of the 3-0  $Z-X$  band is at 150 404.8.

have been discussed for HCl, play an equal or even more important role in the spectrum of HF.

As noted above the  $C^1\Pi$  state can be regarded as the first member of a Rydberg series but higher members of the series were not identified. At higher frequencies, where Rydberg series might be expected to be more easily recognized as a series of features converging to the lowest ionization limit, no series were observed. It is difficult to reconcile the observed optical spectrum with the electron energy loss spectrum reported by Mathur and Hasted (15). None of the principal features of the optical spectrum such as the  $C^1\Pi-X^1\Sigma$  bands occurs in the energy loss spectrum and we can find none of the principal features of the energy loss spectrum in our optical spectrum.

The most unusual bands in the spectrum are those lying beyond the first ionization limit which we have labelled the  $Y$  and  $Z$  bands. The constants of these states are very similar to those of the  $A^2\Sigma$  state of  $HF^+$  (16) and it has been pointed out that the states fit very well as two members of a Rydberg series leading up to the second ionization limit of  $HF^+$  at 19.118 eV which leaves the  $HF^+$  ion in the  $A^2\Sigma$  state (14). From the measurements of the band origins given in Table 24 the effective principal

quantum numbers for the  $Y$  and the  $Z$  states are 2.960 and 3.965. The simple regular behaviour of these bands contrasts sharply with the chaotic appearance of the spectrum below the first ionization limit. The  $Y$  and  $Z$  states are also unusual in that their lifetimes against auto-ionization are much longer than those of most molecular states which are energetically able to autoionize. In the corresponding bands of HCl the auto-ionization rate is so high that no rotational structure is seen (17). It is also interesting to note that the line widths of the bands increase with  $J$  thus indicating that the auto-ionization takes place via a Coriolis interaction with the continuum.

Rather little of the HF spectrum has been analysed even though the resolution of the lines on the plates appears to be sufficient. Further analysis will require either a better theoretical understanding of the excited states or new experimental methods to identify the lines. For the present the spectrum must remain an example of the large gap which exists between the simple model of Rydberg states described in Sect. 4 and the complexity of actual Rydberg states.

#### Acknowledgments

We wish to thank Drs. G. Herzberg and M. L. Ginter for valuable discussions on several aspects of this work and Dr. P. R. Bunker for discussions and calculations on the mixing of states. We are indebted to Professor R. F. Barrow for supplying us with data on the  $B-X$  band system. We also wish to thank Mr. F. Alberti who photographed most of the spectra and Mrs. B. Wadsworth who assisted with the measurements.

TABLE 24. Constants of the  $Y^1\Pi$  and  $Z^1\Pi$  states of HF

State	Vibrational level	$T_0 + G(v)$	$B_v$
$Y^1\Pi$	0	141 672.7	9.96
$Y^1\Pi$	1	142 966.6	9.26
$Y^1\Pi$	2	144 044.0	8.21
$Y^1\Pi$	3	144 864.1	6.87
$Z^1\Pi$	0	147 215.6	8.46
$Z^1\Pi$	1	148 520.7	8.04
$Z^1\Pi$	2	149 591.7	7.22
$Z^1\Pi$	3	150 397.5	5.89

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