Overtone Absorption Bands of Gaseous HF

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With a 21-foot grating, the structure of the 3←0 and 4←0 vibration-rotation absorption bands of gaseous HF was observed and the lines measured. The vibrational constants of the molecules are, using also Imes' measurements of the 1←0 band: $\omega_e=4141.305$, $x_e\omega_e=90.866$, $y_e\omega_e=0.921$. These constants do not permit evaluation of the energy of dissociation, but the simple Birge formula gives rough agreement. Rotational constants are compared with those obtained from the fundamental band and agree, in general, satisfactorily. No evidence of associated molecules is observed in the overtone bands.

In the present communication, measurements of the 3←0 and 4←0 vibration-rotation absorption bands of gaseous HF are described and discussed in some detail; the results of these measurements have been already announced briefly.[1]

The fundamental band of HF was measured by Imes[2] with a plane grating and thermopile and the rotational constants B_e and α_e (in Mulliken's notation[3]) were determined therefrom. The center of this band, at 2.52μ, and the unresolved 2←0 band barely detected at 1.27μ by Schaefer and Thomas[4] were used to obtain the vibrational constants ω_e and $x_e\omega_e$. The resulting value for the anharmonic term seemed to be inconsistent with its value for the other hydrogen halides. It was, therefore, deemed worth while to measure the higher overtone bands of HF in the region where photographic spectroscopy could be employed.

The most satisfactory of various absorption cells was a copper tube 225 cm long, with fluorite windows fastened securely by clamps and high melting point paraffin wax, and with side tubes attached with silver solder.

Hydrogen fluoride was generated[5] by heating KHF_2 in a copper retort which had a sealed-in copper-constantan thermocouple to facilitate control of the rate of heating. This was necessary in order to prevent sputtering of the KHF_2 melt into the retort outlet and to reject the moist gas evolved before the constant boiling mixture is attained (at 504°C).

The spectrograph was a 21-foot, 15,000-line concave grating in a Paschen mount, having a dispersion of 2.64A/mm in the first order region of 8790A and 1.33A/mm in the second order of 6744A. The slit width was 0.04 mm. Eastman infrared sensitive plates, types IP and IN, sensitized in NH_4OH, were used in the region of the 3←0 and 4←0 bands, respectively. A Schott-Jena RG1 filter was used to eliminate higher order radiation below 6000A. Neon lines, as suggested by Meggers and Humphreys,[6] were used for calibration at 8790A and international iron standards at 6744A. Conversion to vacuum wave numbers was made from Kayser[7] and the spectrograms were microphotometered with a Moll, type A instrument.

A 500-watt compact filament projection bulb served as a source of continuous radiation and made possible satisfactory exposures on IP plates in thirty minutes when the cell was empty. Because of clouding and etching of the windows by the HF, exposures of four hours were required with gas at a pressure of *one* atmosphere in the cell. As the time of exposure could not be predetermined, it was found convenient to place several small pieces of plate as test strips next to the whole plate, and to develop a test strip every hour until the correct density was indicated.

A spectrogram of the 3←0 band is shown in Fig. 1 and a microphotometer trace of the same band is given in Fig. 2. No spectrogram or tracing of the 4←0 band satisfactory for reproduction could be obtained.

Nine rotational lines in the positive branch and six in the negative branch of the 3←0

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[1] E. O. Salant and D. E. Kirkpatrick, Phys. Rev. **46**, 318 (1934).

[2] E. S. Imes, Astrophys. J. **50**, 251 (1919).

[3] R. S. Mulliken, Phys. Rev. **36**, 611 (1930).

[4] Schaefer and Thomas, Zeits. f. Physik **12**, 330 (1923).

[5] J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green & Co., 1922), Vol. II, p. 128.

[6] Meggers and Humphreys, Bur. Standards J. Research **10**, 427 (1933).

[7] H. Kayser, *Tabelle der Schwingungszahlen.*

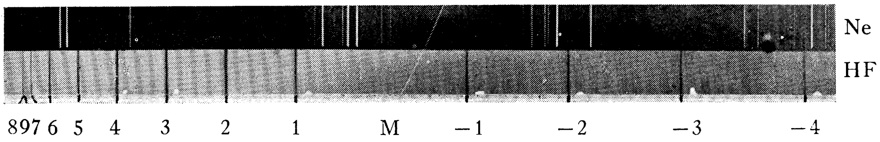

FIG. 1. A portion of the (3←0) band.

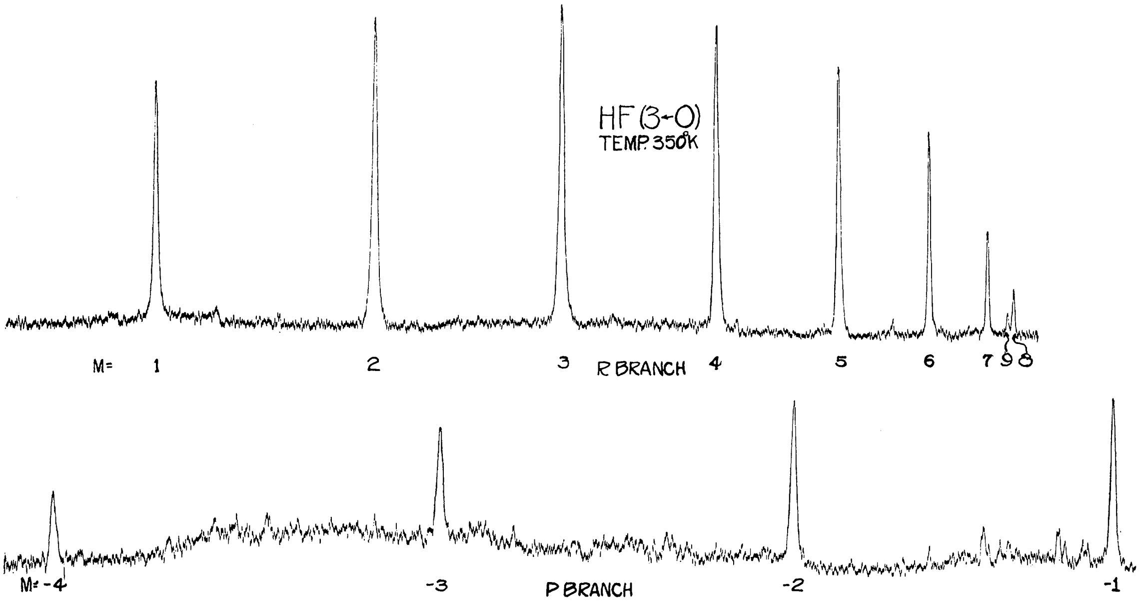

FIG. 2.

band appear. The ninth line of the positive branch appears as a weak line between the seventh and eighth lines, as far as we are aware the only case of reversal of a branch in a non-electronic band. (This is shown more clearly in the microphotometer trace than in the reproduction of the spectrogram.)

Six lines of the positive and five lines of the negative branch of the 4←0 band were observed.

Wave-length and wave number values of the lines of the two bands appear in Table I, together with the values calculated by equations fitted to the measurements by the method of Birge and Shea.[8]

The equations for the band lines are, for the 3←0 band:

$$\nu = 11{,}372.88 + 38.83M - 2.257M^2 - 0.00655M^3, \quad (1)$$

and for the 4←0 band:

$$\nu = 14{,}831.68 + 38.101M - 2.980M^2 - 0.00546M^3, \quad (2)$$

where M is the ordinal number of the line, ±1, ±2, etc.

The values of the molecular constants, calculated from Eqs. (1) and (2), by neglecting the third power terms in $(v+\frac{1}{2})$ and the sixth power terms in $(J+\frac{1}{2})$, are given in Table II, in the notation of Mulliken,[3] Eqs. (2c) to (4c). All values indicated as depending on the 1←0 band have been evaluated with the coefficients of the ordinal numbers calculated by Czerny[9] from Imes' measurements of that band.

The agreement of our values with those found from the 1←0 band is satisfactory, with the exception of β_e, which for the latter band is opposite in sign and several times larger than the values found in the present work.

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[8] Birge and Shea, *A Rapid Method of Calculating the Least Squares Solution of a Polynomial of any Degree* (Univ. of California Press, Berkeley, 1927), p. 93.

[9] M. Czerny, Zeits. f. Physik **45**, 476 (1927).

Table I. *Lines in the two bands in the HF spectrum.*

M	λ_{air} ±0.03A	ν_{vac} ±0.04 cm^{-1}	$\nu_{calc.}$	$\Delta\nu$
(3←0) HF, 8790.42A = 11,372.88 cm^{-1} vac.				
		R BRANCH		
9	8667.08	11534.75	11534.76	−0.01
8	8666.35	11535.72	11535.72	.00
7	8669.29	11531.81	11531.85	− .04
6	8675.80	11523.15	11523.19	− .04
5	8685.88	11509.78	11509.79	− .01
4	8699.55	11491.70	11491.67	+ .03
3	8716.80	11468.95	11468.88	+ .07
2	8737.70	11441.52	11441.46	+ .06
1	8762.26	11409.45	11409.45	.00
		P BRANCH		
−1	8822.32	11331.78	11331.80	− .02
−2	8857.92	11286.24	11286.24	.00
−3	8897.31	11236.27	11236.25	+ .02
−4	8940.49*	11182.00	11181.87	+ .13
−5	8987.57*	11123.43	11123.12	+ .31
−6	9038.94*	11060.21	11060.06	+ .15
(4←0) HF, 6744.67A = 14,831.68 cm^{-1} vac.				
M	λ_{air} ±0.02A	$\nu_{vac.}$ ±0.05 cm^{-1}	$\nu_{calc.}$	$\Delta\nu$
		R BRANCH		
6	6686.36	14951.70	14951.83	−0.13
5	6688.44	14947.05	14947.00	+ .05
4	6693.38	14936.02	14936.05	− .03
3	6701.02	14918.99	14919.02	− .03
2	6711.39	14895.94	14895.92	+ .02
1	6724.55	14866.79	14866.80	− .01
		P BRANCH		
−1	6759.18	14790.62	14790.60	+ .02
−2	6780.74	14743.59	14743.60	− .01
−3	6805.15	14690.70	14690.70	.00
−4	6832.44*	14632.03	14631.95	+ .08
−5	6862.61*	14567.70	14567.36	+ .34

* These lines are very weak and in the case of the (3←0) band occur in a region where there is a paucity of good calibration lines.

The value of 50 cm^{-1} previously listed in the literature for $x_e\omega_e$ obtained by the use of the 1←0 and 2←0 bands, is seen to be very different from any of the values obtained by using any pair of the 1←0, 3←0, and 4←0 bands. This discrepancy is due, presumably, to the insufficient accuracy of the prism-thermopile instrument available to the observers of the 2←0 band.

Calculation of the center of the 1←0 band with the values of ω_e and $x_e\omega_e$ obtained from the 3←0 and 4←0 bands results in a discrepancy of 5 cm^{-1}. It appears to be necessary, therefore, to use a third power term in $(v+\frac{1}{2})$ to account for the centers of these three bands with the accuracy implied by the measurements. The vibrational constants obtained by using all three bands are, then, $\omega_e = 4141.305$ cm^{-1}, $x_e\omega_e = 90.866$ cm^{-1}, $y_e\omega_e = 0.921$ cm^{-1}. The center of the 2←0 band should be, according to these values, at 7752 cm^{-1}, 1.29μ instead of at 1.27μ as found hitherto. A difficulty arises, however, in the calculation of the energy of dissociation. The quantum number at dissociation which one finds with the above values of the vibrational constants appears to have an imaginary value. Whether this is due to an inaccuracy in the determination of the coefficient of the $(v+\frac{1}{2})^3$ term or to the necessity for still higher powers of the vibrational quantum number for a valid description of the upper vibrational levels, cannot be settled definitely although the latter contingency is thought to be the more likely. Attempts, so far, to detect still higher harmonics have failed. The heat of dissociation calculated with the ω_e and $x_e\omega$ obtained from the 3←0 and 4←0 bands, 140 kcal./mole, is seen to agree approximately with

Table II. *Molecular constants of HF.*

ω_e	4134.16 $\left\{\begin{matrix}1\leftarrow0\\3\leftarrow0\end{matrix}\right\}$	4132.32 $\left\{\begin{matrix}1\leftarrow0\\4\leftarrow0\end{matrix}\right\}$	4123.12 $\left\{\begin{matrix}3\leftarrow0\\4\leftarrow0\end{matrix}\right\}$	cm^{-1} vac.
$x_e\omega_e$	85.80 "	84.88 "	83.04 "	cm^{-1} vac.
	(1←0)	(2←0)	(3←0)	(4←0)
Band center, λ	2.52μ	1.29μ calc.	8790.42A	6755.67A air
Band center, ν	3962.56	7751.69 "	11372.88	14831.68 cm^{-1} vac.
B_e	20.925		20.920	20.913 cm^{-1} vac.
B_0	20.543		20.544	20.540 cm^{-1} vac.
α_e	0.7632		0.7523	0.745 cm^{-1} vac.
D_e	−0.00214		−0.00215	−0.00215 cm^{-1} vac.
β_e	−0.000830		+0.000256	0.000314 cm^{-1} vac.
I_e	1.321×10^{-40}		1.322×10^{-40}	1.323×10^{-40} gm cm^2
r_e	0.901×10^{-8}		0.901×10^{-8}	0.901×10^{-8} cm

$$\text{Energy of dissociation} = \frac{(\omega_e - x_e\omega_e)^2}{4x_e\omega_e} = 140 \text{ kcal./mole}$$

the 120 kcal./mole obtained from the data in F_2,[10] H_2,[11] and HF.[12]

An interesting distinction between the anharmonicity factor x_e of HF and that of the other hydrogen halides can be drawn. For HCl[13] this factor is 0.0174, for HBr[14] 0.0171, for HI[15] 0.0172, whereas for HF it is 0.0219. This larger value is reflected, of course, in the greater intensity of the overtone bands of this gas,—very much longer columns of the other hydrogen halides than the 225 cm employed here have yet to reveal a $4\leftarrow 0$ band.[16] It would be interesting if this unusually large anharmonicity should be related, too, to the exceptional readiness of HF molecules to associate. In connection with this matter of association, a spectrogram was taken with the gas at 85°C as well as at 30°C, but no variation in intensity of the lines was observed, contrary to what might be expected from the vapor densities at those temperatures.

We take great pleasure in acknowledging our indebtedness to Dr. R. L. Garman of the Department of Chemistry for the microphotometric tracings.

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[10] Wartenberg, Springer and Taylor, Zeits. f. physik. Chemie, Erganzungsband Bodenstein Festband, 61 (1931).

[11] Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, London, 1932).

[12] Landolt-Börnstein, *Phys-Chem. Tabellen*, p. 1489.

[13] Meyer and Levin, Phys. Rev. **34**, 44 (1929).

[14] Plyler and Barker, Phys. Rev. **44**, 373 (1931).

[15] Nielsen and Nielsen, Phys. Rev. **47**, 585 (1935).

[16] Mr. F. A. Valente of this laboratory reports that examination of the region of the $4\leftarrow 0$ band of HCl, with the 21-foot grating and 50 meters of the gas, showed no trace of absorption.

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Tables for Determining Atomic Wave Functions and Energies

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Tables have been constructed so that wave functions and energies, for any atomic state having $1s$, $2s$ and $2p$ electrons, can be computed by variational means. Exchange terms are included, so that singlet and triplet states can be minimized separately. By using the tables a state can be calculated in a few hours. A few of the possible states have been worked out. The best parameters, the total energies and the term values are given for the states $(1s^2)\,^1S$, $(1s,2s)\,^1S$, ^3S; $(1s,2p)\,^1P$, ^3P; $(1s^2,2s)\,^2S$; $(1s^2,2p)\,^2P$; $(1s^2,2s^2)\,^1S$; $(1s^2,2s,2p)\,^1P$, ^3P; $(1s^2,2p^2)\,^1S$, ^1D, ^3P; $(1s^2,2s^2,2p)\,^2P$; $(1s^2,2s^2,2p^6)\,^1S$; of the atoms He, Li, Be, B, C, N, O, F, Ne, Na and Mg. The intramultiplet separations have been computed, including the spin-spin interaction when necessary: the check with experiment being fairly satisfactory. By the use of an empirical correction rule, term values can be predicted to within a few hundred wave numbers.

The Construction of the Tables

There is a general need for relatively simple wave functions for use in the calculation of atomic properties. In many cases it is more important to have functions expressible in a simple analytic form than it is to have functions as accurate as those of Hartree, for instance. In the hope of partially satisfying this need, the writers have developed a set of tables from which wave functions and energies for a large number of atomic states can be obtained. The variational method is used, and the tables are arranged so that any atomic state containing $1s$, $2s$ and $2p$ electrons can be computed.

Practical considerations governed the choice of the number of parameters used in the trial functions. Four were used in all, one for the $1s$ function, two for the $2s$ and one for the $2p$ functions. While it was realized that an extra parameter in the $2p$ function would give somewhat better results, it was decided that any more than four parameters would greatly increase the complexity of the computations. The tables as finally constructed are easy to use, and the best parameters for any atomic state can be computed in a few hours.

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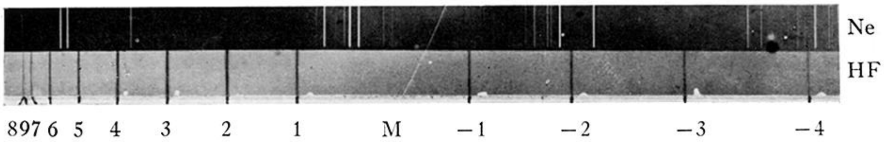

FIG. 1. A portion of the (3←0) band.