

High-Resolution Infrared Emission Spectra of HCl and HF

HCl and HF are important gases for use as absolute wavenumber standards and as media for high-efficiency chemical lasers (1, 2). Recently, HCl has been observed in the infrared region in the upper atmosphere (3) and in the IR absorption spectra of the atmospheres of Venus (4) and an S-type star (5). HCl has been of theoretical interest for the examination of the breakdown of the Born-Oppenheimer approximation (6-8).

References to the previous measurements of the spectra of HF are provided by Hedderich *et al.* (9). For HCl, the room temperature spectrum of the fundamental was recently remeasured by Rinsland *et al.* (10). Other previous absorption measurements of the HCl fundamental were by Guelachvili *et al.* (11) and Rank *et al.* (12), as well as the measurements on hot HCl by Webb and Rao (13). The previous emission measurements were carried out by Clayton *et al.* (14) with a grating spectrometer. The pure rotational lines were measured with a tunable far-infrared laser spectrometer (15) and by submillimeter-wave techniques (16). Finally, a set of Einstein *A* coefficients was recently calculated for HCl and HF (17).

Despite this, relatively few transitions are known for the hydrogen halides. We report here the high-resolution infrared emission spectra of HF and HCl. Vibration-rotation line positions of the $v = 1 \rightarrow 0$ and $v = 2 \rightarrow 1$ bands of hot HF were measured and combined with pure rotational transitions reported previously (9). The $v = 0$ and $v = 1$ pure rotational lines and the $v = 1 \rightarrow 0$, $v = 2 \rightarrow 1$ and the $v = 3 \rightarrow 2$ vibration-rotation bands of H^{35}Cl and H^{37}Cl were observed. In separate least-squares fits, improved sets of molecular constants for HF, H^{35}Cl , and H^{37}Cl were determined. The rotational lines were measured to a precision of better than $\pm 0.0002 \text{ cm}^{-1}$.

The new line positions reported here were measured in two separate experiments. The pure rotational spectrum of HCl, and the rovibrational spectra of HCl and HF, were accidentally recorded while trying to measure the infrared spectrum of CuCl and in the pyrolysis of Freon-22 (CF_2ClH), respectively.

In the first experiment, the pure rotational emission spectrum of HCl was recorded with the Bruker IFS-120HR Fourier transform spectrometer at the University of Waterloo. Solid CuCl was heated to 830°C in a tube furnace. The pumping port was sealed and 5 Torr of argon buffer gas was added to prevent deposition of material on the cell windows. The emission spectrum was recorded at a resolution of 0.005 cm^{-1} over the range 300 - 760 cm^{-1} with a KBr beam splitter and a liquid helium-cooled Si:B detector. The lower wavenumber limit of 300 cm^{-1} was set by the transmission of the KBr beam splitter, while the upper limit was set by a cold 760 cm^{-1} red-pass optical filter. The reaction between hot CuCl and the water impurity present in the system gave HCl as a product.

The rovibrational HCl and HF emission lines were recorded during the measurement of the infrared spectrum of the pyrolysis products of Freon-22 (CF_2ClH) with the Fourier transform spectrometer located at the McMath Solar Telescope on Kitt Peak. A continuous flow of freon was maintained through the tube furnace heated to 1080°C . The total pressure in the system was 0.99 Torr. The unapodized resolution of the spectrometer for this experiment was 0.0099 cm^{-1} with InSb detectors and a KCl beam splitter. The upper wavenumber limit ($\sim 5000 \text{ cm}^{-1}$) was set by a wedged Ge filter.

Our measured line positions are reported in Table I (HF), Table IIa (H^{35}Cl), and Table IIb (H^{37}Cl). The signal-to-noise ratio for the strongest lines was better than 75 for the pure rotational data, and better than 2800 for the vibrational-rotational data.

Data analysis was carried out using PC-DECOMP, a spectral analysis program developed by J. W. Brault. The vibration-rotation HCl and HF data were calibrated using measurements reported previously by Rinsland *et al.* (10). Pure rotational HCl lines were calibrated with CO_2 lines of the ν_2 band which was an impurity in a spectrum of MgCl_2/HCl also measured at the University of Waterloo (18). The CO_2 line positions were taken from the book by Guelachvili and Rao (19).

In separate least-squares fits the line positions for HF, H^{35}Cl , and H^{37}Cl were fit to the usual energy expression (20)

$$E(v, J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + L_v [J(J+1)]^4$$

TABLE I
HF Line Positions in cm⁻¹

v'	J'	v''	J''	Observed	O-C	v'	J'	v''	J''	Observed	O-C
0	1	0	0	41.1109832 ^a	1.0E-06	1	11	0	10	4301.63671 ^b	-7.0E-05
0	2	0	1	82.1711179 ^a	7.0E-08	1	12	0	11	4321.32121 ^b	-1.2E-04
0	3	0	2	123.12967 ^a	-1.0E-05	1	13	0	12	4338.98544 ^b	-1.3E-04
0	4	0	3	163.93616 ^a	-1.0E-05	1	14	0	13	4354.60375 ^b	2.4E-04
0	5	0	4	204.54045 ^a	1.0E-05	1	15	0	14	4368.15167 ^b	1.4E-04
0	6	0	5	244.89283 ^a	1.0E-05	1	16	0	15	4379.60851 ^b	1.1E-04
0	7	0	6	284.94444 ^a	2.4E-04	1	13	1	12	496.68517 ^a	-1.5E-04
0	13	0	12	516.28061 ^a	-8.0E-05	1	14	1	13	531.89851 ^a	-1.2E-04
0	14	0	13	552.92046 ^a	1.6E-04	1	15	1	14	566.46812 ^a	-2.0E-04
0	15	0	14	588.89904 ^a	7.0E-05	1	16	1	15	600.35572 ^a	-1.1E-04
0	16	0	15	624.17733 ^a	2.0E-04	1	17	1	16	633.52402 ^a	1.0E-05
0	17	0	16	658.71682 ^a	1.3E-04	1	18	1	17	665.93707 ^a	-7.0E-05
0	18	0	17	692.48121 ^a	1.8E-04	1	19	1	18	697.56091 ^a	-1.0E-04
0	19	0	18	725.43557 ^a	4.7E-04	1	20	1	19	728.36279 ^a	-1.6E-04
0	20	0	19	757.54540 ^a	-4.0E-05	1	21	1	20	758.31128 ^a	-5.4E-04
0	21	0	20	788.78013 ^a	-8.0E-05	1	22	1	21	787.37827 ^a	1.9E-04
0	22	0	21	819.10918 ^a	-2.0E-05	1	23	1	22	815.5344 ^a	6.4E-04
0	23	0	22	848.50386 ^a	-5.0E-05	1	24	1	23	842.7524 ^a	-9.0E-05
0	24	0	23	876.93745 ^a	-4.0E-05	2	11	1	12	3230.09348 ^b	1.5E-04
0	25	0	24	904.38481 ^a	3.0E-05	2	10	1	11	3282.74768 ^b	-3.0E-05
0	27	0	26	956.22816 ^a	-1.3E-04	2	9	1	10	3334.48637 ^b	8.0E-05
0	28	0	27	980.58320 ^a	6.1E-04	2	8	1	9	3385.25340 ^b	5.0E-05
0	29	0	28	1003.86720 ^a	4.6E-04	2	7	1	8	3434.99221 ^b	-9.6E-04
0	31	0	30	1047.15700 ^a	-1.8E-03	2	6	1	7	3483.65039 ^b	1.0E-04
0	32	0	31	1067.13770 ^a	-2.0E-04	2	5	1	6	3531.16959 ^b	9.0E-05
0	33	0	32	1085.98903 ^a	1.0E-05	2	4	1	5	3577.49618 ^b	6.0E-05
1	14	0	15	3212.78712 ^b	2.9E-03	2	3	1	4	3622.57625 ^b	3.2E-04
1	13	0	14	3269.78406 ^b	-5.2E-04	2	2	1	3	3666.35554 ^b	3.0E-05
1	12	0	13	3326.01911 ^b	-4.5E-04	2	1	1	2	3708.78181 ^b	-3.4E-04
1	11	0	12	3381.43162 ^b	-3.3E-04	2	0	1	1	3749.80427 ^b	1.2E-04
1	10	0	11	3435.96386 ^b	-4.5E-04	2	1	1	0	3827.43237 ^b	-3.5E-04
1	9	0	10	3489.55896 ^b	-7.0E-05	2	2	1	1	3863.94158 ^b	1.0E-05
1	8	0	9	3542.15785 ^b	-7.0E-04	2	3	1	2	3898.85045 ^b	-1.3E-04
1	7	0	8	3593.70541 ^b	3.0E-05	2	4	1	3	3932.11370 ^b	-7.5E-04
1	6	0	7	3644.14227 ^b	-4.0E-05	2	5	1	4	3963.68952 ^b	6.0E-05
1	5	0	6	3693.41248 ^b	4.0E-05	2	6	1	5	3993.53346 ^b	-1.4E-04
1	4	0	5	3741.45946 ^b	8.0E-05	2	7	1	6	4021.60673 ^b	8.0E-05
1	3	0	4	3788.22725 ^b	-1.1E-04	2	8	1	7	4047.87022 ^b	-1.0E-05
1	2	0	3	3833.66122 ^b	-1.2E-04	2	9	1	8	4072.28778 ^b	-1.9E-04
1	1	0	2	3877.70704 ^b	-1.0E-04	2	10	1	9	4094.82538 ^b	-7.0E-05
1	0	0	1	3920.31155 ^b	-2.0E-05	2	11	1	10	4115.45038 ^b	2.0E-05
1	1	0	0	4000.98919 ^b	-5.0E-05	2	15	2	14	544.59319 ^a	-7.0E-05
1	2	0	1	4038.96214 ^b	0.0E+00	2	16	2	15	577.12112 ^a	-3.3E-04
1	3	0	2	4075.29321 ^b	0.0E+00	2	17	2	16	608.94862 ^a	2.3E-04
1	4	0	3	4109.93606 ^b	7.0E-05	2	18	2	17	640.03793 ^a	-1.2E-03
1	5	0	4	4142.84579 ^b	9.0E-05	2	19	2	18	670.36024 ^a	-3.0E-05
1	6	0	5	4173.97944 ^b	1.1E-04	2	20	2	19	699.8808 ^a	1.2E-03
1	7	0	6	4203.29592 ^b	1.7E-04	2	21	2	20	728.5675 ^a	8.5E-04
1	8	0	7	4230.75584 ^b	6.0E-05	2	22	2	21	756.3966 ^a	4.3E-03
1	9	0	8	4256.32233 ^b	5.0E-05	2	23	2	22	783.3306 ^a	1.7E-03
1	10	0	9	4279.96021 ^b	-1.0E-05	2	24	2	23	809.3482 ^a	-2.2E-03

a) From Reference 9.

b) This work; Freon experiment.

TABLE III
HF Rotational Constants in cm^{-1}

Constants	$v = 0$	$v = 1$	$v = 2$
T_v	-	3961.422551(61)	7750.793391(96)
B_v	20.55973027(38)	19.7874707(31)	19.0349573(45)
$D_v \times 10^3$	2.119914(11)	2.063659(41)	2.01001(50)
$H_v \times 10^7$	1.63502(40)	1.5845(41)	1.5301(16)
$L_v \times 10^{11}$	-1.4978(49)	-1.432(41)	-1.351(17)
$M_v \times 10^{15}$	1.049(19)	0.68(28)	-

in which B_v , D_v , H_v , and L_v are the rotational constants. The T_v vibrational term values and the rotational constants were obtained from a linear weighted least-squares fit of the new data reported here with the addition of selected data from published laboratory experiments. Pure rotational HF lines reported by Hedderich *et al.* (9) were included in the fit of our HF lines, and the constants obtained are reported in Table III. Our observed H^{35}Cl and H^{37}Cl lines were combined with pure rotational data (10), and the constants obtained from this fit are reported in Table IV for both isotopomers. For completeness Tables I and II include the line positions taken from the literature.

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TABLE IV
 H^{35}Cl (Upper Entry) and H^{37}Cl (Lower Entry) Rotational Constants
in cm^{-1}

Constants	$v = 0$	1	2	3
T_v	-	2885.976036(37)	5667.982412(57)	8346.776387(75)
	-	2883.870056(49)	5663.926705(73)	8340.926185(99)
B_v	10.44019777(20)	10.13618534(88)	9.8345969(21)	9.5347975(30)
	10.42451455(127)	10.12118972(150)	9.8202849(28)	9.5211500(33)
$D_v \times 10^4$	5.280666(19)	5.214236(53)	5.15410(20)	5.10315(30)
	5.264726(27)	5.198528(121)	5.13863(29)	5.08598(27)
$H_v \times 10^8$	1.66732(37)	1.6133(11)	1.5338(71)	1.4654(84)
	1.65995(62)	1.6059(34)	1.5200(106)	1.3981(59)
$L_v \times 10^{13}$	-8.047(20)	-8.503(68)	-6.96(80)	-
	-8.002(38)	-8.484(308)	-5.68(128)	-

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