NOTES

The Fundamental Bands of H^{35}Cl and H^{37}Cl: Line Positions from High-Resolution Laboratory Data

The purpose of this note is to report accurate measurements of the positions of lines of the (1–0) vibration–rotation bands of H^{35}Cl and H^{37}Cl. The new measurements have been derived from a laboratory spectrum recorded with a Fourier transform spectrometer (FTS) operated at an unapodized spectral resolution of 0.0060 cm^{-1}, where the spectral resolution is defined as $1/(2\Delta)$, with Δ equal to the maximum path difference of 83.02 cm. Molecular constants are reported from a simultaneous least-squares analysis of these measurements and selected infrared and far-infrared data taken from the literature.

The motivation for the present investigation is the need for improved hydrogen chloride line positions for use in IR atmospheric remote sensing investigations. As shown in this work, the HCl line positions on the 1992 HITRAN line parameters compilation (*1*) are significantly in error, especially at high J. The differences can be easily noted because of the wider spectral coverage and improved accuracy of our work in comparison to the most accurate previous study (*2*). Lines with lower-state J up to 13 for H^{35}Cl and up to $J = 12$ for H^{37}Cl have been measured in this work. It is also worth noting that HCl served as a calibration standard in the 1960s and 1970s (*3, 4*), and IR absorption by this molecule has been detected in spectra of the atmospheres of Venus (*5*) and the S-type star R And (*6*).

The spectral data were recorded at room temperature with the Fourier transform spectrometer located in the McMath solar telescope on Kitt Peak. The instrument is operated by the National Solar Observatory (NSO). Two InSb photodiode detectors, a KCl beamsplitter, and a globar source heated to approximately 2000 K were used in the experiment along with a CaF$_2$ prism, which served as a predisperser limiting the spectral bandpass to the 2200–3100 cm^{-1} region. The 45-min integration time produced a spectral signal-to-rms noise of 1500. Dry nitrogen was used to purge the unevacuated paths between the source and the cell and between the cell and the interferometer entrance aperture to reduce the absorption by interfering H$_2$O lines.

The body of the absorption cell used in this study is IN-3 Borosilicate glass with 1-mm-thick optical grade Al$_2$O$_3$ (sapphire) windows wedged at an angle of about 12 arcmin. The 2.58-cm internal diameter cell has an internal optical path length of 2.525 ± 0.01 cm. Prior to filling, the cell was baked at 280 K for 6 hr and

TABLE I

Molecular Constants (in cm^{-1}) for the $v = 0$ and $v = 1$ States of H^{35}Cl and H^{37}Cl

Molecular Constant	H^{35}Cl		H^{37}Cl	
	Value	Uncertainty	Value	Uncertainty
G(1,0)	2.8859760363×10^3	$1.0215594597\times10^{-5}$	2.8838700505×10^3	$7.9118650163\times10^{-6}$
B(0)	1.0440198110×10^1	$3.8393263710\times10^{-7}$	1.0424515107×10^1	$2.8190901705\times10^{-7}$
D(0)	$5.2807588762\times10^{-4}$	$7.9476389598\times10^{-9}$	$5.2648617004\times10^{-4}$	$5.8676898731\times10^{-8}$
H(0)	$1.6736638813\times10^{-8}$	$5.1408993638\times10^{-11}$	$1.6682673233\times10^{-8}$	$3.8892378556\times10^{-11}$
L(0)	$8.7079238726\times10^{-13}$	$4.6561010673\times10^{-14}$	$8.9403983490\times10^{-13}$	$3.4842198016\times10^{-14}$
B(1)	1.0136181632×10^1	$6.4562766806\times10^{-7}$	1.0121186316×10^1	$5.6309195217\times10^{-7}$
D(1)	$5.2137299704\times10^{-4}$	$9.4050599023\times10^{-9}$	$5.1981013520\times10^{-4}$	$8.6508673868\times10^{-9}$
H(1)	$1.6055186193\times10^{-8}$	$4.6586780764\times10^{-11}$	$1.5986709552\times10^{-8}$	$3.8239455668\times10^{-11}$
L(1)	$8.3169244312\times10^{-13}$	$3.8137407344\times10^{-14}$	$8.2789544238\times10^{-13}$	$3.3712613775\times10^{-14}$
Weighted Error	9.99×10^{-6}		7.22×10^{-6}	

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TABLE II

Experimental Line Positions[a] for H^{35}Cl

v'	J'	v"	J"	Measured Position	Res	U	v'	J'	v"	J"	Measured Position	Res	U
0	1	0	0	20.878284[b]	0.00	0.02	1	1	0	2	2843.624158	0.25	0.20
0	2	0	1	41.743895[b]	-0.02	0.03	1	0	0	1	2865.097721	-0.31	0.20
0	3	0	2	62.584183[b]	0.01	0.03	1	1	0	0	2906.246352	0.38	0.20
0	4	0	3	83.386501[b]	-0.01	0.03	1	2	0	1	2925.896078	0.02	0.20
0	5	0	4	104.138260[b]	-0.01	0.03	1	3	0	2	2944.913000	0.16	0.20
0	6	0	5	124.826909[b]	0.03	0.04	1	4	0	3	2963.284896	0.12	0.20
0	7	0	6	145.439949[b]	0.02	0.04	1	5	0	4	2980.999803	-0.14	0.20
0	8	0	7	165.964971[b]	0.08	0.05	1	6	0	5	2998.045986	-0.37	0.20
0	9	0	8	186.389616[b]	-0.01	0.07	1	7	0	6	3014.411893	-0.69	0.20
0	10	0	9	206.701655[b]	-0.09	0.06	1	8	0	7	3030.086294	-0.13	0.20
1	28	0	29	2087.2320[c]	4.26	26.06	1	9	0	8	3045.057974	0.05	0.20
1	26	0	27	2152.0722[c]	16.02	23.31	1	10	0	9	3059.316154	0.63	0.21
1	25	0	26	2184.1148[c]	-1.99	26.40	1	11	0	10	3072.850059	-0.00	0.46
1	23	0	24	2247.3922[c]	-10.64	23.68	1	12	0	11	3085.649412	-1.00	1.11
1	22	0	23	2278.6016[c]	-8.62	25.74	1	13	0	12	3097.703981	-3.57	3.25
1	21	0	22	2309.5056[c]	-27.18	27.29	1	14	0	13	3109.0027[c]	-19.87	22.90
1	20	0	21	2340.0958[c]	-22.98	25.29	1	15	0	14	3119.5412[c]	2.30	24.44
1	19	0	20	2370.3566[c]	-23.27	26.06	1	16	0	15	3129.3011[c]	-27.63	23.31
1	18	0	19	2400.2755[c]	-23.01	25.99	1	17	0	16	3138.2833[c]	-10.10	23.79
1	17	0	18	2429.8403[c]	-12.98	26.73	1	18	0	17	3146.4710[c]	-25.18	24.18
1	16	0	17	2459.0357[c]	-13.95	23.98	1	19	0	18	3153.8616[c]	-13.68	23.31
1	15	0	16	2487.8490[c]	-19.76	25.58	1	20	0	19	3160.4413[c]	-31.03	24.72
1	14	0	15	2516.2667[c]	-31.46	24.12	1	21	0	20	3166.2094[c]	-4.35	24.44
1	13	0	14	2544.2779[c]	-23.50	23.37	1	22	0	21	3171.1490[c]	-25.37	25.00
1	12	0	13	2571.868408	-2.76	5.50	1	23	0	22	3175.2586[c]	-34.46	24.05
1	11	0	12	2599.021447	-1.62	1.40	1	26	0	25	3182.5346[c]	-9.62	26.06
1	10	0	11	2625.725335	-1.30	0.79	1	27	0	26	3183.2495[c]	-21.82	27.86
1	9	0	10	2651.966649	-0.40	0.32	1	28	0	27	3183.1018[c]	-12.11	27.68
1	8	0	9	2677.731754	0.27	0.20	1	29	0	28	3182.0837[c]	1.70	26.24
1	7	0	8	2703.007066	0.14	0.20	1	31	0	30	3177.4153[c]	61.83	32.97
1	6	0	7	2727.779199	0.28	0.20	1	32	0	31	3173.7463[c]	31.27	39.98
1	5	0	6	2752.034666	0.16	0.20	1	33	0	32	3169.1882[c]	38.27	32.33
1	4	0	5	2775.760103	-0.19	0.20	1	35	0	34	3157.3654[c]	-27.23	73.72
1	3	0	4	2798.942287	-0.13	0.20	1	36	0	35	3150.0841[c]	-169.07	73.72
1	2	0	3	2821.567988	-0.09	0.20							

a) Measured line positions are in cm^{-1}, "Res" is the residual (measured minus calculated) in 10^{-4} cm^{-1} obtained with the constants given in Table I, and U is the estimated 1σ uncertainty in 10^{-4} cm^{-1}.

b) These measurements are taken from Ref. (14).

c) These measurements are taken from Ref. (15).

then conditioned with 21 Torr of HCl overnight. Hydrogen chloride gas certified to 99.999% purity at purchase was used to fill the cell to a pressure of 1.84 Torr ($\pm 2\%$) with a gas handling system that used MKS Baratron capacitance manometers. According to the (1–0) band measurements of Pine and Fried (7), which cover $R(10)$ to $P(10)$ for H^{35}Cl and $R(8)$ to $P(8)$ for H^{37}Cl, the magnitude of the self-induced pressure-shifts is 3.8×10^{-5} cm^{-1} or less at this pressure. We corrected our measured positions for pressure shifts based on the gas pressure and the self-induced pressure-shift coefficients in Ref. (7). No corrections were applied for lines outside the range of the data in Ref. (7).

Line positions were derived by least-squares fitting an ~ 0.5-cm^{-1} interval centered on each absorption line. A Voigt lineshape was assumed (see Refs. (8–10) for a description of the analysis method) along with the self-broadening coefficients measured by Pine and Fried (7). The HCl positions were calibrated from measurements of 11 lines of the ^{12}C^{16}O$_2$ ν_3 band between $P(4)$ and $R(52)$. As illustrated in Fig. 1 of the paper by Malathy Devi et al. (11), these lines show two overlapping absorption components in Kitt Peak FTS spectra: a broad component formed at ambient atmospheric pressure (~ 600 Torr) in the purged paths and a narrow component formed at low pressure (~ 0.02 Torr) in the evacuated interferometer tank. Our measured positions of the narrow absorption component were calibrated with respect to the positions reported

TABLE III

Experimental Line Positions[a] for H ^{37}Cl

v'	J'	v"	J"	Measured Position	Res	U	v'	J'	v"	J"	Measured Position	Res	U
0	1	0	0	20.846923[b]	-0.01	0.02	1	4	0	5	2773.823906	-0.09	0.20
0	2	0	1	41.681215[b]	-0.01	0.03	1	3	0	4	2796.969606	-0.14	0.20
0	3	0	2	62.490255[b]	-0.00	0.03	1	2	0	3	2819.560056	-0.07	0.20
0	4	0	3	83.261445[b]	0.00	0.03	1	1	0	2	2841.582218	0.14	0.20
0	5	0	4	103.982226[b]	0.02	0.03	1	0	0	1	2863.023094	-0.32	0.20
0	6	0	5	124.640084[b]	0.03	0.04	1	1	0	0	2904.110379	0.35	0.20
0	7	0	6	145.222562[b]	0.02	0.04	1	2	0	1	2923.731539	0.04	0.20
0	8	0	7	165.717277[b]	-0.03	0.05	1	3	0	2	2942.721325	0.05	0.20
0	9	0	8	186.111934[b]	-0.05	0.05	1	4	0	3	2961.067587	0.03	0.20
0	10	0	9	206.394337[b]	0.09	0.07	1	5	0	4	2978.758404	0.04	0.20
1	28	0	29	2086.4332[c]	-14.54	23.57	1	6	0	5	2995.782022	-0.25	0.20
1	27	0	28	2118.9189[c]	-11.31	33.35	1	7	0	6	3012.126968	-0.44	0.20
1	26	0	27	2151.1662[c]	22.02	22.36	1	8	0	7	3027.782010	0.02	0.20
1	25	0	26	2183.1560[c]	13.97	23.98	1	9	0	8	3042.735977	0.06	0.29
1	24	0	25	2214.8806[c]	8.75	24.11	1	10	0	9	3056.978135	0.60	0.61
1	23	0	24	2246.3271[c]	0.19	25.99	1	11	0	10	3070.497744	0.07	1.38
1	22	0	23	2277.4843[c]	0.67	23.06	1	12	0	11	3083.284630	0.09	3.25
1	21	0	22	2308.3370[c]	-15.90	25.16	1	13	0	12	3095.328610	-0.34	11.07
1	20	0	21	2338.8764[c]	-10.26	24.69	1	14	0	13	3106.6170[c]	-29.79	25.49
1	19	0	20	2369.0897[c]	18.24	26.73	1	15	0	14	3117.1460[c]	-30.64	23.06
1	18	0	19	2398.9556[c]	-13.60	23.45	1	16	0	15	3126.9042[c]	-23.97	22.82
1	17	0	18	2428.4714[c]	-1.81	22.36	1	18	0	17	3144.0703[c]	-8.40	24.69
1	16	0	17	2457.6180[c]	-5.47	24.55	1	19	0	18	3151.4597[c]	-11.85	22.71
1	15	0	16	2486.3827[c]	-18.77	23.98	1	20	0	19	3158.0439[c]	-6.50	23.19
1	14	0	15	2514.7535[c]	-28.15	24.40	1	21	0	20	3163.8140[c]	-1.73	23.31
1	13	0	14	2542.7136[c]	-67.46	30.16	1	22	0	21	3168.7607[c]	-13.60	25.16
1	12	0	13	2570.2626[c]	-6.05	24.11	1	23	0	22	3172.8787[c]	-20.81	25.16
1	11	0	12	2597.371618	2.22	6.92	1	24	0	23	3176.1611[c]	-20.66	24.11
1	10	0	11	2624.031411	0.09	2.77	1	28	0	27	3180.7993[c]	43.37	34.12
1	9	0	10	2650.229711	0.07	1.11	1	29	0	28	3179.7984[c]	13.40	28.64
1	8	0	9	2675.952865	0.75	0.46	1	30	0	29	3177.9235[c]	-15.93	31.62
1	7	0	8	2701.187184	0.11	0.22	1	31	0	30	3175.1784[c]	47.92	70.71
1	6	0	7	2725.919428	0.21	0.20	1	34	0	33	3161.5875[c]	-32.61	70.71
1	5	0	6	2750.136108	0.13	0.20							

a)   Measured line positions are in cm^{-1}, "Res" is the residual (measured minus calculated) in 10^{-4} cm^{-1} obtained with the constants given in Table I, and U is the estimated 1σ uncertainty in 10^{-4} cm^{-1}.

b)   These measurements are taken from Ref. (14).

c)   These measurements are taken from Ref. (15).

by Guelachvili and Rao (12), scaled by 0.999999785, the mean of the two multiplicative factors determined by Brown and Toth (13). As a check, we compared the assumed ^{12}C^{16}O$_2$ positions with the positions determined by Malathy Devi et al. (11), which were calibrated with respect to the well-determined $P(7)$ $F1(2) \leftarrow F2(2)$ transition of the ν_3 ^{12}CH$_4$ fundamental band. For the 34 lines measured in Ref. (11), the average difference (Ref. (11) minus 0.999999785 times Ref. (12)) is -6.5×10^{-6} cm^{-1}. Based on the accuracy and consistency of the calibration data and the consistency of our ^{12}C^{16}O$_2$ measurements with respect to the calibration data, we estimate that the uncertainty in the absolute wavenumber calibration of our HCl positions is less than ± 0.0002 cm^{-1}.

The line positions were analyzed by modeling the measurements with the expression

$$\nu(v', J', v'', J'') = G(v', v'') + E(v', J') - E(v'', J''),   \quad (1)$$

where $\nu(v', J', v'', J'')$ is the transition frequency corresponding to vibrational and rotational quantum numbers v', J' in the upper state and v'', J'' in the lower state, $G(v', v'')$ is the vibrational term difference between the upper and lower states, and $E(J')$ and $E(J'')$ are the rotational term values in the upper and lower states, respectively. The rotational term values have been computed from the usual energy expression for a $^1\Sigma$ diatomic molecule.

TABLE IV

Comparison of Positions (cm^{-1}) for Selected Transitions in the (1–0) Bands of $H^{35}Cl$ and $H^{37}Cl$

Rotational Transition	Isotopic Species	Measured (This Work)	This Work- HITRAN 1992[a]	This Work- Ref.(2)
P(12)	$H^{35}Cl$	2599.021447	-0.019905	
	$H^{37}Cl$	2597.371618	-0.018316	
P(5)	$H^{35}Cl$	2775.760103	-0.001169	
	$H^{37}Cl$	2773.823906	-0.001092	
P(1)	$H^{35}Cl$	2865.097721	-0.000546	-0.001179
	$H^{37}Cl$	2863.023094	-0.000711	-0.000906
R(5)	$H^{35}Cl$	2998.045986	-0.002985	-0.001114
	$H^{37}Cl$	2995.782022	-0.002820	-0.000978
R(12)	$H^{35}Cl$	3097.703981	-0.040259	-0.000419
	$H^{37}Cl$	3095.328610	-0.038537	-0.001090

[a] Ref. (1).

$$E(v, J) = B(v)J(J + 1) - D(v)J^2(J + 1)^2 + H(v)J^3(J + 1)^3 - L(v)J^4(J + 1)^4, \qquad (2)$$

where $B(v)$, $D(v)$, $H(v)$, and $L(v)$ are the rotational constants to be determined. The $G(1, 0)$ vibrational term difference and the upper and lower state rotational constants have been obtained from a weighted linear least-squares fit of the Kitt Peak measurements and additional data selected from reported laboratory experiments. The two additional datasets included were the pure rotation measurements of Nolt et al. (14) and the high-J (1–0) vibration–rotation band emission measurements of Clayton et al. (15). Each measurement was assigned a weight given by $1/\sigma^2$, where σ is the estimated uncertainty. The uncertainties for the far-IR data were taken as given in Ref. (14). The uncertainties of the high-J IR data from Clayton et al. (15) were computed from the weights given in Ref. (15) with unit weight assigned an uncertainty equal to 0.0025 cm^{-1}. This value was quoted in Ref. (15) as the measurement accuracy for unblended lines. The uncertainties of the Kitt Peak data were computed with the formula given by Reuter et al. (16). A minimum uncertainty of 2×10^{-5} cm^{-1} was adopted to obtain a realistic weighting of the far-IR and IR datasets.

Table I presents the molecular constants and their 1σ uncertainties obtained from the least-squares analysis. The number of digits given in the table is sufficient to reproduce all of the calculated wavenumbers to better than 1×10^{-6} cm^{-1}. Fits to the data with higher order terms in the rotational term-value expansion were tried, but the values obtained for the higher-order coefficients were not statistically significant. At the bottom of Table I, we also give the weighted fitting error $(N \sum w_i \delta_i^2 / m \sum w_i)^{1/2}$, where N is the number of lines, m is the number of degrees of freedom, and δ_i is the observed-minus-calculated wavenumber for line i (16).

Table II presents the $H^{35}Cl$ measurements and the residuals of the weighted least-squares best fit to the data. Results for $H^{37}Cl$ are given in the same format in Table III. For most lines, the residual (measured minus calculated) position is less than the estimated 1σ uncertainty.

Table IV lists for selected lines the difference between our measured position and the calculated value in the 1992 HITRAN compilation (1) and the difference between our measurement and the measurement by Guelachvili et al. (2). Our positions are systematically about 0.001 cm^{-1} lower than those of Guelachvili et al. (2). This difference is consistent with the quoted absolute calibration accuracy of $4 \times 10^{-7} \times \nu$ for the data in Ref. (2), where ν is the measured position in cm^{-1}. The difference between the Kitt Peak measurement and the 1992 HITRAN compilation value (1) increases rapidly with increasing J. According to Ref. (1), the HITRAN positions and lower state energies were calculated from the parameters of Coxon and Ogilvie (17). However, an incorrect sign for the Dunham coefficient Y_{22} was used as input data for the HITRAN calculations (1). The correct calculated positions can be found in Table 5 of Ref. (17), and these values are within 0.001 cm^{-1} of our measurements.

The present work provides accurate measured positions and rovibrational constants which can be used to compute improved positions for the $H^{35}Cl$ and $H^{37}Cl$ (1–0) vibration–rotation infrared bands. A new global fit of HCl data, similar to the work of Ref. (17), would be worthwhile, since we have not included all of the reported measurements in our analysis. For example, $H^{35}Cl$ and $H^{37}Cl$ hot band measurements extending to high J in the $\Delta v = 1$ sequence (15) and high temperature absorption measurements of $H^{35}Cl$ (18) and $H^{37}Cl$ (19, 20) have not been considered.

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