NOTE

The 7–0 Overtone Spectrum of HCl

The ground state potential energy function of HCl plays an important role in molecular physics and chemical dynamics. HCl is a popular target molecule for the testing of *ab initio* methods and the potential is useful in the interpretation of a variety of experiments ranging from femtosecond dynamics to the study of product distributions in chemical reactions. Recent experimental work on HCl includes the refinement of the dissociation energy $D_0(H^{35}Cl) = 35\,748.2(8)\,cm^{-1}$ by threshold ion-pair production spectroscopy (*1*) and the measurement of new submillimeter-wave pure rotational line positions (*2, 3*). Coxon and Hajigeorgiou (*4*) have fitted all of the available HCl and DCl ground state data using a parameterized potential energy function and Parekunnel *et al.* (*5*) have determined a new set of Dunham constants for low vibrational levels of HCl and DCl. Both of these papers also determined corrections needed to account for the breakdown of the Born–Oppenheimer approximation.

The experimental ground state potential (*4*) is determined from two types of data: low-v data (from pure rotation and vibration–rotation transitions) and high-v data (from the $B^1\Sigma^+–X^1\Sigma^+$ electronic transition). The low-v data end at $v = 3$ (from the 3–2 band) from the emission lines of LeBlanc *et al.* (*6*) with a precision of about $0.0002\,cm^{-1}$ and $v = 6$ (from the 6–5 band) from Clayton *et al.* (*7*) with a precision of about $0.0025\,cm^{-1}$. The high-v data cover the range from $v = 7$ to 17 with a large number of bands in the $B^1\Sigma^+–X^1\Sigma^+$ transition with a precision of $0.025\,cm^{-1}$. The $v = 17$ level lies about $1450\,cm^{-1}$ from the dissociation limit (*4*). Unfortunately the low-v and high-v data do not connect, although the entire data set can be fitted with a parameterized potential function (*4*). There is a gap in the data between $v = 0$–6 and $v = 7$–17 because the high-v data are known with respect to $v' = 0$ of the $B^1\Sigma^+$ state, not $v'' = 0$ of the $X^1\Sigma^+$ state.

During a recent visit to the National Solar Observatory we noticed that the necessary measurements to put the high-v data on the same energy scale as the low-v data have already been made, but the line positions were never published. In two papers, the 4–0, 5–0, 6–0, and 7–0 overtone bands were analyzed to determine the self-pressure-broadening coefficients (*8*) and the linestrengths (*9*). We have, therefore, measured the 7–0 band and report here on the line positions.

The 7–0 overtone band of HCl was recorded by J. Gelfand, M. Zughul, and J. Brault on December 4, 1978 with the Fourier transform spectrometer associated with the McMath–Pierce Solar Telescope of the National Solar Observatory. A 6-m base path White cell was filled with 991 Torr of HCl and the total path length was set to 408 m. The spectrometer had a silver beamsplitter and was operated with Si photodiode detectors and a Corion 560-nm (17800–18150 cm^{-1}) bandpass filter. The resolution of the spectrometer was $0.048\,cm^{-1}$ and 60 scans were co-added in 2 hours of integration.

The line positions were measured with the PC-Decomp program of J. Brault. Each feature was fitted with a Voigt line shape function and the positions are reported in Table 1. Unfortunately no calibration lines were recorded and, in any case, the band was measured at a single HCl pressure of more than one atmosphere. The line positions are therefore subject to an unknown pressure shift of perhaps $\pm0.02\,cm^{-1}$ as well as a calibration error of perhaps $\pm0.01\,cm^{-1}$ for a total absolute accuracy of about ±0.025. This is essentially the same accuracy as the vacuum UV data of the $B^1\Sigma^+–X^1\Sigma^+$ transition. The line positions were fitted with the usual energy-level expression

$$F_v(J) = T_v + B_v J(J + 1) - D_v[J(J + 1)]^2$$

and the constants are provided in Table 2. The ground state constants were fixed to the values of LeBlanc *et al.* (*6*).

The spectroscopic constants (Table 2) can be compared with the values calculated by Coxon and Hajigeorgiou (*4*) from their fitted potential. For $H^{35}Cl$ their T_7 value is $0.040\,cm^{-1}$ higher than ours while for $H^{37}Cl$ the discrepancy is $0.055\,cm^{-1}$. The calculated B_7 and D_7 values are also in reasonable agreement with the direct observations (Table 2). The particularly good agreement between the observed and calculated band origins is a testament to the power and predictive value of potential fitting. Interestingly the $v = 7$ level of HCl was also seen recently by Lin *et al.* (*10*). They observed the 7–6 emission band of HCl at low resolution from the 193-nm photolysis of CH_2CHCl.

TABLE 1
Line Positions (in cm^{-1}) in the 7–0 Overtone Transition of HCl

	7-0 H^{35}Cl				7-0 H^{37}Cl			
J	R(J)	O-C	P(J)	O-C	R(J)	O-C	P(J)	O-C
0	18050.506	-0.009			18039.024	0.012		
1	18062.965	0.005	18012.969	0.000	18051.436	-0.011	18001.519	0.001
2	18071.154	-0.018	17987.902	0.009	18059.650	-0.009	17976.511	0.028
3	18075.150	0.010	17958.609	-0.023	18063.610	-0.028	17947.268	-0.007
4	18074.845	-0.011	17925.199	-0.002	18063.350	-0.025	17913.908	0.001
5	18070.298	-0.012	17887.633	0.017	18058.858	-0.002	17876.401	0.007
6	18061.500	0.005	17845.901	0.010	18050.092	0.006	17834.766	0.013
7	18048.398	-0.007	17800.052	0.008	18037.047	0.001		
8	18031.020	-0.011			18019.728	-0.003		
9	18009.377	0.008						

TABLE 2

Spectroscopic Constants for the $v = 7$ Vibrational Level of the $X^1\Sigma^+$ State of HCl

Constants	H^{35}Cl		H^{37}Cl	
	Present values	Coxon & Hajigeorgiou (4)	Present values	Coxon & Hajigeorgiou (4)
T_v	18033.84731(460)	18033.887	18022.36486(552)	18022.420
B_v	8.334826(257)	8.335721	8.324435(387)	8.324828
$10^4 \times D_v$	4.9233(247)	5.01848	4.9270(447)	5.00322

Note. Numbers in parentheses are one standard deviation in the last digits quoted.

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