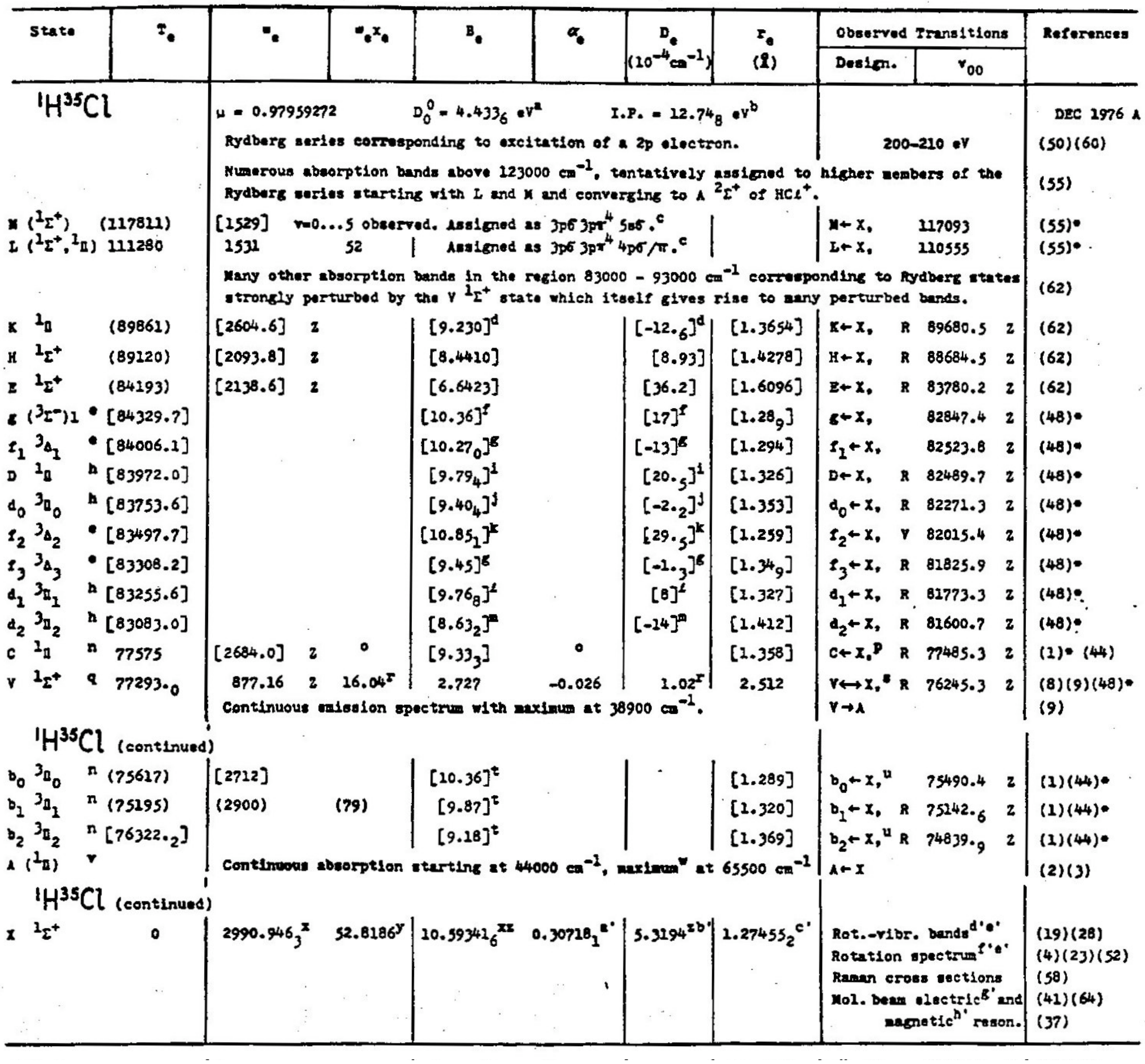
Appendix B: **Molecular Constants for $^{1}H^{35}Cl$**

The following literature[1] data for $^{1}H^{35}Cl$ is listed from highest energy electronic state to lowest energy electronic state, which means that the ground electronic state is listed last (it is designated with the symbol $^{1}\Sigma^{+}$). Many of the rotational and vibrational constants are given in the footnotes.



State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	D_e (10^{-4} cm^{-1})	r_e (Å)	Observed Transitions		References
								Design.	ν_{00}	
$^{1}H^{35}Cl$		μ = 0.97959272 D_0^0 = 4.433$_6$ eV^{a} I.P. = 12.74$_8$ eV^{b}								DEC 1976 A
		Rydberg series corresponding to excitation of a 2p electron.						200–210 eV		(50)(60)
		Numerous absorption bands above 123000 cm^{-1}, tentatively assigned to higher members of the Rydberg series starting with L and M and converging to A $^{2}\Sigma^{+}$ of HCl^{+}.								(55)
M ($^{1}\Sigma^{+}$)	(117811)	[1529]	v=0...5 observed. Assigned as $3p\sigma\, 3p\pi^4\, 5s\sigma$.^{c}					M ← X,	117093	(55)*
L ($^{1}\Sigma^{+}$, $^{1}\Pi$)	111280	1531	52	Assigned as $3p\sigma\, 3p\pi^4\, 4p\sigma/\pi$.^{c}				L ← X,	110555	(55)*
		Many other absorption bands in the region 83000 – 93000 cm^{-1} corresponding to Rydberg states strongly perturbed by the V $^{1}\Sigma^{+}$ state which itself gives rise to many perturbed bands.								(62)
K $^{1}\Pi$	(89861)	[2604.6] z		$[9.230]^{d}$		$[-12._{6}]^{d}$	[1.3654]	K ← X, R	89680.5 z	(62)
H $^{1}\Sigma^{+}$	(89120)	[2093.8] z		[8.4410]		[8.93]	[1.4278]	H ← X, R	88684.5 z	(62)
E $^{1}\Sigma^{+}$	(84193)	[2138.6] z		[6.6423]		[36.2]	[1.6096]	E ← X, R	83780.2 z	(62)
g ($^{3}\Sigma^{-}$)1	^{e} [84329.7]			$[10.36]^{f}$		$[17]^{f}$	$[1.28_{9}]$	g ← X,	82847.4 z	(48)*
f_1 $^{3}\Delta_1$	^{e} [84006.1]			$[10.27_{0}]^{g}$		$[-13]^{g}$	[1.294]	f_1 ← X,	82523.8 z	(48)*
D $^{1}\Pi$	^{h} [83972.0]			$[9.79_{4}]^{i}$		$[20._{5}]^{i}$	[1.326]	D ← X, R	82489.7 z	(48)*
d_0 $^{3}\Pi_0$	^{h} [83753.6]			$[9.40_{4}]^{j}$		$[-2._{2}]^{j}$	[1.353]	d_0 ← X, R	82271.3 z	(48)*
f_2 $^{3}\Delta_2$	^{e} [83497.7]			$[10.85_{1}]^{k}$		$[29._{5}]^{k}$	[1.259]	f_2 ← X, V	82015.4 z	(48)*
f_3 $^{3}\Delta_3$	^{e} [83308.2]			$[9.45]^{g}$		$[-1._{3}]^{g}$	$[1.34_{9}]$	f_3 ← X, R	81825.9 z	(48)*
d_1 $^{3}\Pi_1$	^{h} [83255.6]			$[9.76_{8}]^{l}$		$[8]^{l}$	[1.327]	d_1 ← X, R	81773.3 z	(48)*
d_2 $^{3}\Pi_2$	^{h} [83083.0]			$[8.63_{2}]^{m}$		$[-14]^{m}$	[1.412]	d_2 ← X, R	81600.7 z	(48)*
C $^{1}\Pi$	^{n} 77575	[2684.0] z	^{o}	$[9.33_{3}]$	^{o}		[1.358]	C ← X,^{p} R	77485.3 z	(1)* (44)
V $^{1}\Sigma^{+}$	^{q} 77293.$_{0}$	877.16 z	16.04^{r}	2.727	-0.026	1.02^{r}	2.512	V ↔ X,^{s} R	76245.3 z	(8)(9)(48)*
		Continuous emission spectrum with maximum at 38900 cm^{-1}.						V → A		(9)
$^{1}H^{35}Cl$ (continued)										
b_0 $^{3}\Pi_0$	^{n} (75617)	[2712]		$[10.36]^{t}$			[1.289]	b_0 ← X,^{u}	75490.4 z	(1)(44)*
b_1 $^{3}\Pi_1$	^{n} (75195)	(2900)	(79)	$[9.87]^{t}$			[1.320]	b_1 ← X, R	75142.$_{6}$ z	(1)(44)*
b_2 $^{3}\Pi_2$	^{n} [76322.$_{2}$]			$[9.18]^{t}$			[1.369]	b_2 ← X,^{u} R	74839.$_{9}$ z	(1)(44)*
A ($^{1}\Pi$)	^{v}	Continuous absorption starting at 44000 cm^{-1}, maximum^{w} at 65500 cm^{-1}						A ← X		(2)(3)
$^{1}H^{35}Cl$ (continued)										
X $^{1}\Sigma^{+}$	0	2990.946_{3}^{x}	52.8186^{y}	10.59341_{6}^{zz}	$0.30718_{1}^{a'}$	$5.3194^{zb'}$	$1.27455_{2}^{c'}$	Rot.-vibr. bands$^{d'e'}$ Rotation spectrum$^{f'e'}$ Raman cross sections Mol. beam electric$^{g'}$ and magnetic$^{h'}$ reson.		(19)(28) (4)(23)(52) (58) (41)(64) (37)

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[1] Huber, K. P. and Herzberg, G., *Molecular Spectra & Molecular Structure IV: Constants of Diatomic Molecules"*, Van Nostrand, New York (1979), p.284-287.

$^1H^{35}Cl$:

[a] From $D_0^0(H_2)$, $D_0^0(Cl_2)$, and $\Delta H_{f0}^0(HCl)$.

[b] From the photoelectron spectrum (33)(38)(46); photoionization measurements give similar results (20)(27). A somewhat smaller I.P.(12.73_0 eV) may be derived from the second band system in the photoelectron spectrum at 16.25_4 eV corresponding to A $^2\Sigma^+$ of HCl^+. Higher ionization potentials at 207.1 and 208.7 eV correspond to the removal of a 2p electron (50).

[c] Strongly broadened by preionization (lifetime 1.1×10^{-14}s)(55).

[d] Average B, D values; $B(R,P) - B(Q) = + 0.385$.

[e] Configuration $\ldots\sigma^2\pi^3 4p\pi$.

[f] Average B, D values; $B(1^+) - B(1^-) = - 0.06_0$.

[g] Refers to Δ^+; Q branch not resolved.

[h] Configuration $\ldots\sigma^2\pi^3 4p\sigma$.

[i] Average B, D values; $B(\Pi^+) - B(\Pi^-) = + 0.063$.

[j] Average B, D values; $B(\Pi^+) - B(\Pi^-) = - 0.04_0$.

[k] Average B, D values; $B(\Delta^+) - B(\Delta^-) = - 0.03_0$.

[l] Average B, D values; $B(\Pi^+) - B(\Pi^-) = - 0.16_0$.

[m] Average B, D values; $B(\Pi^+) - B(\Pi^-) = - 0.06_7$.

[n] Configuration $\ldots\sigma^2\pi^3 4s\sigma$.

[o] $v=1,2,3$ are increasingly diffuse; $B_1 = 9.29_6$. (44) give $\omega_e = 2817.5$, $\omega_e x_e = 66.0$, $B_e = 9.44$, $\alpha_e = 0.15$.

[p] Also observed in inert matrices (57).

[q] Typical "V" state with configuration $\ldots\sigma\pi^4\sigma^*$.

[r] $\omega_e y_e = 0.113_3$; $\beta_e = 0.2_0 \times 10^{-4}$.

[s] Very extended progression in absorption, not yet analyzed in detail. The higher vibrational levels are strongly perturbed by Rydberg states (48)(62). The vibrational and rotational constants given were obtained from the emission spectrum with $v \leq 3$ (8)(9) but because of the perturbations have only very limited meaning.

[t] Diffuse rotational structure; 1-0 and 2-0 are increasingly diffuse.

[u] The $b_2 \leftarrow X$ and $b_0 \leftarrow X$ components have only 1/50 of the intensity of $b_1 \leftarrow X$.

[v] Configuration $\ldots\sigma^2\pi^3\sigma^*$.

[w] Absorption coefficient $k=40$.

$^1H^{35}Cl$ (continued):

[x] Applying the Dunham corrections (28) obtain $\omega_e = 2991.0904$ and $B_e = 10.593553$. Additional corrections (adiabatic, non-adiabatic) discussed by (49). Vibrational levels up to $v=5$ have been observed in infrared absorption (12)(19)(28) and emission (10), higher levels in the $V \rightarrow X$ bands (8)(9). Dunham potential coefficients (61). Most recent <u>ab initio</u> values of the ground state molecular constants (59); charge distribution (40).

[y] $\omega_e y_e = + 0.2243_7$, $\omega_e z_e = - 0.0121_8$ (28).

[z] Slightly different constants in (11)(26)(31). These papers and (39) give also constants for $H^{37}Cl$.

[a'] $+ 0.001772_4(v+\frac{1}{2})^2 - 0.0001201(v+\frac{1}{2})^3$.

(*) [b'] $+(- 7.51_0 \times 10^{-6})(v+\frac{1}{2}) + 4.0_0 \times 10^{-7}(v+\frac{1}{2})^2$; higher order terms in (28). See also (30). $\beta_e < 0$

[c'] Uncorrected value from the $B_e(= Y_{01})$ given in the table. The internuclear distance at the minimum of the Born-Oppenheimer curve is $r_e = 1.2746149$ Å (49)(63).

[d'] Absolute intensities ($cm^{-2}atm^{-1}$) of the

1-0 band:	130	(5)
2-0 band:	2.9	(5)
	3.70	(17)(45)
3-0 band:	0.023	(5)

[e'] Pressure-induced shifts (by foreign gases) of rotation-vibration and rotation lines (13)(14)(21)(22)(24). For discussions of pressure-induced bands and pure rotation lines ($\Delta J=2$) see (32)(36). Self and foreign-gas line broadening (5)(7)(16)(17)(18)(29)(43)(45)(47)(52). Infrared absorption in liquid and solid phases (42)(51).

[f'] Absolute intensity measurements (25)(34).

[g'] $\mu_{el}(v=0,1,2) = 1.1085, 1.1390, 1.1685$ D, resp. (41). Dipole moment function (41)(54); see also (53)(56). $g_J = 0.4594$, also quadrupole and other hyperfine coupling constants (41)(64); see also (35)(53).

[h'] Proton spin - rotation interaction constant (15)(37).