© 2000 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 73, 321—327 (2000)

Analysis of the Infrared Spectrum of RbCl Vapor

John F. Ogilvie, [#] **Hiromichi Uehara,*** **and Koui Horiai,**

Department of Chemistry, Faculty of Science, Josai University, Keyakidai, Sakado, Saitama 350-0295

(Received September 14, 1999)

With laser diodes we measured spectra of RbCl vapor near 1000 K in absorption in a region 43800—46400 m^{-1} and assigned vibration-rotational transitions, 226 of $^{85}Rb^{35}Cl$ up to $v' = 9$ and $J' = 160$, 158 transitions of $^{85}Rb^{37}Cl$ and 125 of $^{87}Rb^{35}Cl$, all with $\Delta v = 2$. We made a global fit of these 509 new data plus 28 published pure rotational transitions. Of eight evaluated parameters, six are adjusted, pertaining to a function for potential energy, and two are constrained, pertaining to nonadiabatic rotational effects; these parameters suffice to reproduce these data generally within uncertainties of their measurement. Comparison is made with corresponding spectral parameters of HCl, LiCl, NaCl and KCl.

Spectral measurements on vapors over solid rubidium chloride, reported before our experiments, comprise narrow lines in two sets in microwave[1] and millimetre-wave[2] regions and a broad feature at resolution 1100 m^{-1} in the far-infrared region.[3] Rotational parameters were well defined from the former data,[1,2] but vibrational parameters from the two regions apparently differ: Deduced indirectly from millimetre-wave lines, $\omega_e = 23334$ m^{-1} and $\omega_e x_e = 85.6$ m^{-1} whereas deduced from the infrared feature, $\omega_e = 22800 \pm 600$ m^{-1} and $\omega_e x_e = 92$ m^{-1}; no disparity exists when estimated error, arising from poor spectral resolution in infrared spectra, is taken into account. Other available data from spectral measurements comprise the electric dipolar moment from the Stark effect[4] and rotational g factor from the Zeeman effect;[5] the latter experiments were subsequently conceded to be susceptible to systematic error.[6]

A laser diode can emit lines in the far infrared region lines of effective width of order 0.1 m^{-1}, or about 10^{-4} the effective spectral slit width of the earlier spectrometer;[3] such a device is hence well suited to resolve individual lines in vibration-rotational spectra of RbCl diatomic molecules, for which the interval between adjacent lines near a centre of a band is about 16 m^{-1}, to an extent that lines from separate bands do not grossly overlap. The spectrum is further congested by the presence of RbCl in isotopic variants of appreciable abundance; with atomic relative abundances at ^{85}Rb 0.7215, ^{87}Rb 0.2785, ^{35}Cl 0.75529, and ^{37}Cl 0.24471, the molecular abundances are $^{85}Rb^{35}Cl$ 0.545, $^{85}Rb^{37}Cl$ 0.177, $^{87}Rb^{35}Cl$ 0.21, and $^{87}Rb^{37}Cl$ 0.068. Bands of all but the latter isotopic variant are thus expected to make significant contributions to total intensity within the same general region of the absorption spectrum.

To improve available spectral data of RbCl, we undertook measurements of the far-infrared spectrum in a sequence with $\Delta v = 2$; although lines for these transitions corresponding to the first overtone of the fundamental band, and other members of the same sequence with vibrational quantum number v'' up to 7, are likely to be much less intense than lines in the fundamental band and its sequence with $\Delta v = 1$, our available diodes operated in the former spectral region, not the latter. As a result of these measurements we assigned measured lines to 509 transitions of RbCl in three isotopic variants; we combined these data with 28 published frequencies of lines for pure rotational transitions, and obtained a satisfactory global fit with only six adjusted parameters in a function for potential energy. Here we describe our measurements and results, and compare parameters derived for RbCl with those of four chlorides of other elements in group 1 of the periodic chart.

Experimental

The apparatus for these measurements is the same as that described in our previous papers,[7,8] except that the system to acquire data is replaced with one having improved precision. In summary, the spectrometer is equipped with tunable diode lasers (Spectra-Physics or Laser Photonics, SP5000), two detectors (copper-doped germanium, CuGe, cooled with liquid helium) and a cylindrical vessel to contain sample vapors in the path of an infrared beam reflected back and forth between mirrors according to a design of White type. The central portion of this vessel, on the floor of which we placed crystals of RbCl, is heated to a required temperature. Frequency modulation (1 kHz) is applied to the laser source and the resulting absorption signal was 2f-detected with a phase-sensitive detector. The spectrometer is controlled with a computer (Compaq Deskpro 5133) equipped with AD and DA converters (Contec, 16 bits). Because we remove fringes and high-frequency noise with Fourier manipulation of the spectrum[7,9] large temporal coefficients ('time constants') are unnecessary for phase-sensitive detection of signals. To sweep a full width of a segment of the spectrum, typically 70 m^{-1}, requires 35 s with temporal coefficient 10 ms which is the smallest available with our spectrometer.

We charged a White cell with crystalline RbCl (50 g) that we had heated under vacuum about 520 K for one day to remove adsorbed water vapor. For measurements of spectral absorption

---

Permanent address: Centre for Experimental and Constructive Mathematics, Simon Fraser University, Burnaby, BC V5A IS6 Canada; ogilvie@cecm.sfu.ca.

we maintained the temperature about the centre of the cell within a range 990—1030 K. We admitted dinitrogen buffer gas (2700 Pa) to minimize migration of sample vapor from a heated zone of the cell. The heated zone and the mirror mounts are thermally insulated by systems with cool water mounted near the end of the heated zone of the cell. The inner wall of the cell is lined with a wick (stainless-steel mesh). With 40 traversals of the multipass cell for laser radiation the length of optical path is 40 m, although the actual path in which RbCl molecules existed in significant concentration was shorter.

For calibration we used lines of SO_2 [J. W. C. Johns, personal communication to H. Uehara, 1987] and BrCl.[10] The procedure consists of measurements of two successive scans in each set, i.e. etalon and RbCl plus reference gas. Measurements of spectra are made within segments of a range 43800—46400 m^{-1} according to characteristics of available laser diodes and calibration lines. Figure 1 shows a portion of the diode laser spectrum of RbCl with assigned lines. A final fit of assigned lines indicates that effective precision of measurements is 0.15 m^{-1} for most lines; 55 other lines are retained in the data set, with uncertainty 0.50 m^{-1}, in cases of overlapped lines in congested regions, which are indicated with an asterisk in Table 1.

Assignment of Spectral Lines

On the basis of spectral parameters from microwave spectra,[1,2] we predicted wave numbers of vibration-rotational lines in the region of the first overtone and other bands in the same sequence. When we undertook measurements in regions expected for band heads, we found that our predictions were sufficiently near observable features that further measurements could be conducted on that basis. We transferred digitized diode laser spectra thus observed to computers (IBM 300XL and NEC PC-H98 model 100) with which we processed all spectra with Fourier manipulation (routines written with Visual Basic 5.0 under Windows NT) and assigned spectral transitions from Loomis–Wood diagrams (Basic under OS/2).

Fringes and high-frequency noise are eliminated according to a criterion[7] to truncate an array in Fourier space. Because spectral lines are those of transitions with $\Delta v = 2$, the ratio of signal to noise is small for most lines; Loomis–Wood diagrams hence enabled us to discern spectral series near band heads in R branches upon which preliminary assignments were made.

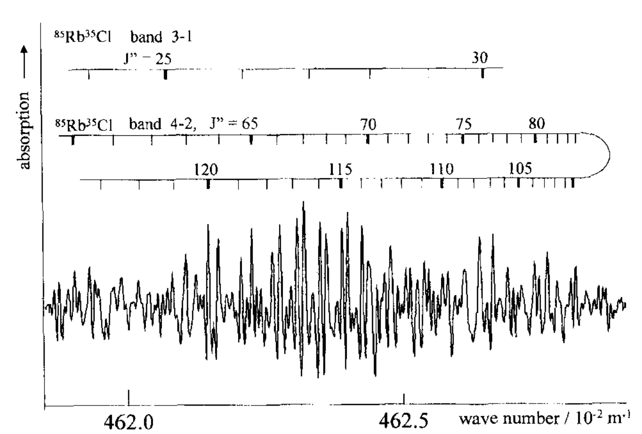

Fig. 1. Absorption spectrum of RbCl vapour near the head of band 4–2, indicating lines of $^{85}Rb^{35}Cl$ assigned near that head and also lines of band 3–1.

Wave numbers of lines for pure known rotational and these vibration-rotational transitions became input to programme Radiatom,[11] which yielded tentative values of parameters and more extensive tables of predicted wave numbers. Analysis was thus extended to P branches and proceeded in an iterative manner until most distinct spectral features in recorded spectra were identified and results were self-consistent. In total, 509 lines were assigned to bands in sequences with $\Delta v = 2$ for variants with 226 lines for $^{85}Rb^{35}Cl$, 158 for $^{85}Rb^{37}Cl$, and 125 for $^{87}Rb^{35}Cl$, combined in an analysis with pure rotational transitions 16 for $^{85}Rb^{35}Cl$, 6 for $^{85}Rb^{37}Cl$, and 6 for $^{87}Rb^{35}Cl$, all listed in Table 1.

The function for effective potential energy is[11,12]

$$\begin{aligned} V(z) &= hcc_0 z^2 \Big(1 + \sum_{j=1}^{4} c_j z^j\Big) \\ &\quad + h^2[1 + m_e(t_0^{Rb}/M^{Rb} + t_0^{Cl}/M^{Cl})](M^{Rb} + M^{Cl})J(J+1)(2-z)^2 \\ &\quad /[(8\pi^2 M^{Rb} M^{Cl}) R_e^2 (2+z)^2], \end{aligned} \tag{1}$$

in which c_j, $0 \leq j \leq 4$, are coefficients of z^{j+2} in a radial function for potential energy; t_0^{Rb} and t_0^{Cl} are coefficients of z^0 for specified atomic centres in an analogous expansion for nonadiabatic rotational effects; h is Planck's constant; c is the speed of light; m_e, M^{Rb}, and M^{Cl} are masses of electron, rubidium, and chlorine atoms, respectively; R_e is equilibrium internuclear separation. The argument of this function is a reduced displacement parameter

$$z = 2(R - R_e)/(R + R_e). \tag{2}$$

Six parameters c_j, $0 \leq j \leq 4$, and R_e were adjusted to fit 537 pure rotational and vibration-rotational transitions, whereas t_0^{Rb} and t_0^{Cl} were fixed to reproduce known values of the equilibrium electric dipolar moment[4] and rotational g factor;[5] although the latter value is suspect,[6] an empirical estimate[13] of g_r yields a similar value, which was accordingly used. Spectral measurements are somewhat insensitive to particular values of t_0^{Rb} and t_0^{Cl}: attempts to define their values through fitting yielded inconclusive results; for this reason fixed values were adopted instead. With parameters of RbCl listed in Table 2 residuals between observed and calculated wave numbers of all transitions showed only random distribution; a value 0.993 of the normalised standard deviation of the fit indicates that uncertainties of measurements are properly assigned. An extended table of calculated wave numbers, residuals and ratio of residual to assigned uncertainty for all assigned lines in microwave and infrared spectra is available from the authors upon request.

Discussion

Notable features of this vibration-rotational spectrum of RbCl vapour are the heads of bands that lie within an accessible range of measurement. For band 4–2 of $^{85}Rb^{35}Cl$ a head appears about 46289 m^{-1} corresponding to $J'' = 92$; lines on either side of this value of J were measured, extending

Table 1. Measured Rotational and Vibration-Rotational Transitions of RbCl[a)]

			$^{85}Rb^{35}Cl$						$^{87}Rb^{35}Cl$		
v'	J'	v''	J''	ν/m^{-1}	$\delta\nu/m^{-1}$	v'	J'	v''	J''	ν/m^{-1}	$\delta\nu/m^{-1}$
0	1	0	0	17.4827343	0.0000020	0	1	0	0	17.3656760	0.0000040
0	34	0	33	593.63592	0.00033	0	30	0	29	520.44358	0.00033
0	35	0	34	611.04766	0.00033	0	34	0	33	589.66614	0.00033
0	42	0	41	732.80913	0.00033	0	41	0	40	710.64773	0.00033
0	49	0	48	854.32576	0.00033	1	28	1	27	483.30395	0.00033
1	1	1	0	17.3922788	0.0000100	1	38	1	37	655.42226	0.00033
1	21	1	20	365.05501	0.00033						
1	34	1	33	590.56019	0.00033				$^{85}Rb^{37}Cl$		
1	35	1	34	607.88180	0.00033						
1	42	1	41	729.00960	0.00033	0	35	0	34	587.72713	0.00033
1	49	1	48	849.89249	0.00033	0	36	0	35	604.47251	0.00033
2	1	2	0	17.3020997	0.0000133	0	42	0	41	704.85819	0.00033
2	34	2	33	587.49410	0.00033	1	35	1	34	584.74086	0.00033
2	35	2	34	604.72509	0.00033	1	36	1	35	601.40095	0.00033
3	34	3	33	584.43705	0.00033	2	35	2	34	581.76357	0.00033
3	35	3	34	601.57851	0.00033						

							$^{85}Rb^{35}Cl$							
v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}
2	34	0	35	45438.27*	2	35	0	36	45415.12	2	36	0	37	45391.47
2	38	0	39	45342.87	2	39	0	40	45318.46	2	48	0	49	45090.43
2	49	0	50	45064.59	2	83	0	84	44070.82	2	84	0	85	44038.58
2	85	0	86	44006.31	3	19	1	20	45435.98	3	20	1	21	45415.12
3	21	1	22	45394.41*	3	23	1	24	45351.26*	3	25	1	26	45307.08
3	34	1	35	45102.61	3	36	1	37	45055.16	3	73	1	74	44052.28
3	75	1	76	43991.25	3	84	1	85	43708.92*	3	85	1	86	43676.79*
3	23	1	22	46167.74	3	25	1	24	46193.91	3	26	1	25	46206.39
3	27	1	26	46218.97	3	28	1	27	46231.29	3	29	1	28	46243.05
3	30	1	29	46255.27	3	31	1	30	46266.90	4	1	2	2	45446.22*
4	2	2	3	45427.64	4	3	2	4	45410.37	4	4	2	5	45392.72*
4	7	2	8	45337.47*	4	8	2	9	45318.46	4	19	2	20	45100.33
4	20	2	21	45079.51	4	21	2	22	45058.56	4	22	2	23	45036.90
4	61	2	62	44073.06	4	62	2	63	44044.39	4	64	2	65	43987.77
4	74	2	75	43692.78	4	78	2	79	43570.34	4	79	2	80	43538.86
4	24	2	23	45841.43	4	26	2	25	45866.93	4	27	2	26	45879.45
4	28	2	27	45891.50	4	58	2	57	46172.91	4	59	2	58	46179.22
4	61	2	60	46191.56	4	62	2	61	46197.78	4	63	2	62	46203.37
4	64	2	63	46209.25	4	65	2	64	46214.44	4	66	2	65	46219.74
4	67	2	66	46224.67	4	68	2	67	46229.54	4	69	2	68	46234.10
4	70	2	69	46238.58	4	71	2	70	46242.75	4	72	2	71	46247.04
4	73	2	72	46250.82	4	74	2	73	46254.39	4	75	2	74	46258.04
4	76	2	75	46261.21	4	77	2	76	46264.16	4	79	2	78	46269.87
4	80	2	79	46272.59	4	81	2	80	46274.85	4	82	2	81	46277.24
4	83	2	82	46278.98	4	85	2	84	46282.44	4	103	2	102	46278.98
4	105	2	104	46274.85	4	106	2	105	46272.59	4	107	2	106	46269.87
4	108	2	107	46266.90	4	109	2	108	46264.16	4	111	2	110	46257.07
4	112	2	111	46253.53	4	113	2	112	46249.96	4	115	2	114	46241.59
4	116	2	115	46237.46	4	117	2	116	46232.81	4	118	2	117	46228.10
4	119	2	118	46223.25	4	120	2	119	46218.06	4	121	2	120	46212.81
4	122	2	121	46207.19	4	123	2	122	46201.70	4	124	2	123	46195.36
4	156	2	155	45902.64*	4	158	2	157	45878.47*	4	159	2	158	45865.22
4	160	2	159	45852.13	5	4	3	5	45057.55	5	26	3	27	44618.06
5	49	3	50	44067.89	5	50	3	51	44041.87	5	51	3	52	44015.53
5	52	3	53	43989.48	5	62	3	63	43716.40	5	63	3	64	43688.15
5	67	3	68	43573.21	5	68	3	69	43544.06	5	69	3	70	43514.87
5	10	3	9	45307.71	5	11	3	10	45322.88	5	12	3	11	45338.17*
5	13	3	12	45352.70	5	16	3	15	45396.49	5	17	3	16	45410.37
5	18	3	17	45424.42	5	19	3	18	45438.27	5	60	3	59	45846.06
5	63	3	62	45863.85	5	64	3	63	45869.21	5	65	3	64	45874.68
5	66	3	65	45879.87	5	67	3	66	45884.75	5	68	3	67	45889.59
5	69	3	68	45894.16	5	70	3	69	45898.51	5	71	3	70	45902.64
5	72	3	71	45906.76	5	114	3	113	45904.33	5	115	3	114	45900.20
5	116	3	115	45895.80	5	117	3	116	45891.50	5	118	3	117	45886.68
5	119	3	118	45881.72	5	120	3	119	45876.42	5	121	3	120	45871.11

Table 1. (Continued)

v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}
5	122	3	121	45865.22	5	123	3	122	45859.73	5	124	3	123	45853.85
5	125	3	124	45847.77	5	126	3	125	45841.43	6	10	4	11	44614.39
6	36	4	37	44060.99	6	37	4	38	44037.40	6	38	4	39	44013.33*
6	39	4	40	43989.48	6	50	4	51	43714.05	6	51	4	52	43688.15
6	55	4	56	43582.32	6	57	4	58	43528.33	6	14	4	13	45033.18
6	15	4	14	45047.59	6	16	4	15	45062.38*	6	17	4	16	45076.33
6	18	4	17	45090.43*	6	36	4	35	45309.30	6	38	4	37	45329.74
6	39	4	38	45339.54	6	40	4	39	45349.76	6	45	4	44	45396.09*
6	46	4	45	45405.15	6	47	4	46	45413.71	6	48	4	47	45422.35
6	49	4	48	45430.56	6	50	4	49	45438.27	6	51	4	50	45446.22
6	134	4	133	45444.14	6	135	4	134	45435.98	6	136	4	135	45427.64
6	137	4	136	45419.41	6	138	4	137	45411.10*	6	139	4	138	45402.30*
6	140	4	139	45393.30*	6	144	4	143	45354.71	6	145	4	144	45344.58
6	148	4	147	45313.70*	7	21	5	22	44066.17	7	22	5	23	44044.95*
7	24	5	25	44002.84	7	25	5	26	43981.52	7	37	5	38	43710.64
7	38	5	39	43686.56	7	42	5	43	43590.33	7	44	5	45	43541.06
7	45	5	46	43516.17	7	41	5	40	45025.83	7	42	5	41	45035.07
7	43	5	42	45044.17	7	44	5	43	45053.64	7	45	5	44	45062.38
7	47	5	46	45079.51	7	48	5	47	45087.83	7	49	5	48	45096.08
7	50	5	49	45104.22	7	135	5	134	45098.65	7	136	5	135	45090.43
7	137	5	136	45082.10	7	138	5	137	45073.51	7	139	5	138	45064.59
7	140	5	139	45055.46	7	141	5	140	45045.96	8	5	6	6	44049.47
8	6	6	7	44031.23	8	7	6	8	44013.33*	8	8	6	9	43994.55
8	9	6	10	43976.22	8	23	6	24	43697.87*	8	24	6	25	43676.79
8	28	6	29	43590.33	8	30	6	31	43546.38	8	31	6	32	43523.92
8	150	6	149	44619.11*	8	151	6	150	44608.00*	9	11	7	10	44001.20
9	12	7	11	44015.53	9	14	7	13	44044.81	9	15	7	14	44058.91
9	16	7	15	44073.06	9	85	7	84	44601.61	9	86	7	85	44602.92
9	87	7	86	44603.97	9	91	7	90	44606.13	9	92	7	91	44606.13
9	93	7	92	44606.13	9	97	7	96	44603.97	9	98	7	97	44602.92
9	99	7	98	44601.61										
							$^{85}Rb^{37}Cl$							
2	11	0	12	45062.38	2	12	0	13	45043.27	2	69	0	70	43692.78*
2	73	0	74	43578.05	2	74	0	75	43549.30	3	17	1	18	44621.33
3	18	1	19	44601.61	3	43	1	44	44053.39	3	57	1	58	43700.96
3	58	1	59	43674.48	3	61	1	62	43594.16	3	5	1	4	45029.44
3	7	1	6	45060.79	4	29	2	30	44051.28	4	44	2	45	43708.92
4	45	2	46	43684.64	4	49	2	50	43586.40	4	30	2	29	45044.17
4	31	2	30	45055.76	4	60	2	59	45308.76	4	62	2	61	45320.95
4	63	2	62	45326.17*	4	65	2	64	45337.47	4	66	2	65	45342.87
4	68	2	67	45352.70	4	77	2	76	45388.77	4	78	2	77	45391.47
4	80	2	79	45397.32	4	82	2	81	45402.30	4	84	2	83	45406.17*
4	85	2	84	45408.42	4	87	2	86	45411.78	4	88	2	87	45413.00
4	90	2	89	45415.12	4	93	2	92	45416.78	4	96	2	95	45416.78
4	99	2	98	45415.12	4	101	2	100	45413.71	4	103	2	102	45411.10
4	107	2	106	45403.23	4	108	2	107	45401.13	4	109	2	108	45398.50
4	110	2	109	45396.09	4	111	2	110	45393.30	4	121	2	120	45354.71
4	122	2	121	45349.76	4	123	2	122	45344.58	4	124	2	123	45339.54
4	126	2	125	45328.39	4	127	2	126	45322.88	4	128	2	127	45316.72
4	158	2	157	45051.28	4	159	2	158	45039.92	4	160	2	159	45028.12
5	13	3	14	44054.59	5	31	3	32	43688.15*	5	36	3	37	43577.13
5	38	3	39	43531.62	5	21	3	20	44610.20	5	68	3	67	45025.83
5	69	3	68	45030.38	5	70	3	69	45035.07*	5	72	3	71	45043.27
5	74	3	73	45051.28*	5	75	3	74	45054.23	5	77	3	76	45060.79
5	78	3	77	45064.08	5	80	3	79	45070.03	5	82	3	81	45074.79
5	85	3	84	45080.71	5	86	3	85	45082.10	5	87	3	86	45083.73
5	88	3	87	45084.98	5	89	3	88	45085.96	5	91	3	90	45087.83
5	93	3	92	45088.54	5	94	3	93	45088.54	5	96	3	95	45088.54
5	97	3	96	45088.54	5	98	3	97	45087.83	5	100	3	99	45085.96
5	101	3	100	45084.98	5	102	3	101	45083.73	5	104	3	103	45080.71
5	107	3	106	45074.79	5	109	3	108	45070.03	5	113	3	112	45058.56
5	114	3	113	45055.16	5	115	3	114	45051.28	5	116	3	115	45047.59
5	117	3	116	45043.27	5	119	3	118	45035.07	5	120	3	119	45030.38
5	121	3	120	45025.83	6	14	4	15	43716.40	6	15	4	16	43697.87*
6	16	4	17	43678.42	6	21	4	22	43580.09	6	24	4	25	43519.31
6	1	4	0	43997.64	6	2	4	1	44013.88	6	3	4	2	44029.93

Table 1. (Continued)

v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}	v'	J'	v''	J''	ν/m^{-1}
6	5	4	4	44060.99	6	53	4	52	44610.67	6	54	4	53	44618.06
6	135	4	134	44613.62	6	136	4	135	44606.13	7	3	5	4	43596.72
7	4	5	5	43579.63	7	7	5	8	43527.32	7	1	5	0	43679.31
7	2	5	1	43695.05	7	23	5	22	43993.51	7	26	5	25	44029.93
7	27	5	26	44041.72	7	28	5	27	44053.39	7	29	5	28	44064.81
7	158	5	157	44070.82	7	159	5	158	44059.11	7	161	5	160	44035.64*
8	12	6	11	43529.47	8	13	6	12	43544.06*	8	15	6	14	43571.18
8	16	6	15	43585.19	8	23	6	22	43675.91	8	24	6	23	43688.15*
8	25	6	24	43699.98	8	26	6	25	43711.76	8	54	6	53	43976.22
8	55	6	54	43983.21	8	56	6	55	43990.05	8	58	6	57	44002.84
8	59	6	58	44009.26	8	64	6	63	44037.40	8	66	6	65	44047.82
8	67	6	66	44052.64	8	68	6	67	44057.35	8	69	6	68	44061.84
8	70	6	69	44066.39	8	118	6	117	44066.17	8	119	6	118	44061.84
8	120	6	119	44057.23	8	121	6	120	44052.28	8	123	6	122	44041.87*
8	124	6	123	44037.40*	8	125	6	124	44031.35	8	128	6	127	44013.88
8	130	6	129	44001.20	8	131	6	130	43994.55	8	132	6	131	43987.77
8	133	6	132	43981.52*	9	57	7	56	43678.22*	9	58	7	57	43684.64
9	59	7	58	43691.10	9	60	7	59	43696.95	9	61	7	60	43703.00
9	62	7	61	43708.56	9	63	7	62	43714.05					
^{87}Rb^{35}Cl														
2	28	0	29	45428.61	2	29	0	30	45406.17*	2	32	0	33	45337.47
2	33	0	34	45313.70*	2	44	0	45	45047.59	2	80	0	81	44028.37
2	81	0	82	43997.11	3	11	1	12	45447.37*	3	12	1	13	45428.61*
3	13	1	14	45408.42	3	14	1	15	45388.77	3	16	1	17	45348.39*
3	17	1	18	45328.39	3	30	1	31	45049.07	3	31	1	32	45025.83
3	68	1	69	44062.97	3	69	1	70	44033.30	3	71	1	72	43974.32
3	80	1	81	43699.98	3	11	1	10	45844.67	3	12	1	11	45859.73
3	13	1	12	45874.68	3	14	1	13	45889.59	3	15	1	14	45904.33
4	13	2	14	45074.79	4	14	2	15	45055.16	4	15	2	16	45035.07*
4	57	2	58	44044.81	4	59	2	60	43990.05	4	69	2	70	43705.81
4	70	2	71	43676.79	4	1	2	0	45348.39	4	4	2	3	45398.50
4	5	2	4	45415.12	4	6	2	5	45430.56*	4	7	2	6	45447.37*
4	37	2	36	45841.43	4	38	2	37	45852.13	4	39	2	38	45862.06
4	40	2	39	45872.34	4	41	2	40	45881.72	4	42	2	41	45891.50
5	44	3	45	44055.61	5	45	3	46	44030.83	5	21	3	20	45316.72
5	22	3	21	45329.74	5	23	3	22	45342.87	5	27	3	26	45392.72
5	28	3	27	45405.15	5	29	3	28	45416.78	5	30	3	29	45428.61
5	31	3	30	45440.25	6	30	4	31	44059.11	6	31	4	32	44037.10*
6	32	4	33	44013.88	6	33	4	34	43991.24	6	45	4	46	43704.71
6	46	4	47	43679.66	6	24	4	23	45022.74	6	25	4	24	45035.07*
6	26	4	25	45047.59*	6	53	4	52	45313.70	6	54	4	53	45321.47
6	55	4	54	45328.39	6	56	4	55	45335.17	6	57	4	56	45341.61
6	58	4	57	45348.39	6	59	4	58	45354.71	6	66	4	65	45394.41
6	67	4	66	45399.19	6	69	4	68	45408.42	6	70	4	69	45413.00
6	71	4	70	45416.78	6	72	4	71	45420.95	6	74	4	73	45428.61
6	75	4	74	45431.53*	6	76	4	75	45435.24	6	77	4	76	45438 27
6	78	4	77	45441.26	6	79	4	78	45444.14	6	80	4	79	45446.22
6	107	4	106	45443.24	6	108	4	107	45440.25	6	109	4	108	45437.35
6	110	4	109	45434.16	6	111	4	110	45430.56*	6	112	4	111	45427.64
6	114	4	113	45419.41*	6	116	4	115	45411.10	6	118	4	117	45402.30
6	119	4	118	45397.32	6	127	4	126	45351.26*	6	128	4	127	45344.58*
6	129	4	128	45338.17	6	130	4	129	45331.16	6	132	4	131	45316.72
6	133	4	132	45309.30	7	14	5	15	44067.89*	7	15	5	16	44047.82
7	16	5	17	44028.37	7	18	5	19	43988.41	7	31	5	32	43711.76
7	36	5	37	43597.13	7	37	5	38	43573.89	7	38	5	39	43550.21
7	39	5	40	43526.78	7	67	5	66	45066.16	7	68	5	67	45070.80
7	70	5	69	45079.51	7	71	5	70	45083.73	7	72	5	71	45087.83
7	73	5	72	45091.39	7	75	5	74	45098.65	7	76	5	75	45101.65
7	109	5	108	45102.61	7	111	5	110	45096.08	7	112	5	111	45092.57
7	113	5	112	45088.54	7	114	5	113	45084.98	7	115	5	114	45080.71
7	116	5	115	45076.33	7	117	5	116	45072.08	7	119	5	118	45062.46
7	120	5	119	45057.55	8	2	6	1	44046.51					

a) Rotational transitions with uncertainty $\delta\nu = 0.00033\ \mathrm{m}^{-1}$ from Ref. 2; other rotational transitions from Ref. 1; uncertainties of vibration-rotational transitions $\delta\nu = 0.15\ \mathrm{m}^{-1}$ except $0.50\ \mathrm{m}^{-1}$ for wave numbers marked with asterisk.

Table 2. Spectral and Other Parameters of Diatomic Chlorides MCl of Elements M = H, Li, Na, K, and Rb[a)]

	HCl	LiCl	NaCl	KCl	RbCl
Data[b)]	2+1054	68+2509	17+1206	22+354	28+509
$v_{\max}$	7	8	8	4	9
c_0/m^{-1}	21114061.87±1.59	14628136.9±5.7	15247257.0±18.1	15243691±550	15533158.6±33.5
c_1	−1.3634522±0.0000056	−1.7197929±0.0000047	−2.076785±0.000037	−2.22777±0.00120	−2.296891±0.000056
c_2	0.865491±0.000028	1.694040±0.000027	2.54160±0.00027	2.1329±0.0181	2.84703±0.00057
c_3	−0.47092±0.00035	−0.95168±0.00027	−1.8567±0.0020	2.686±0.140	−1.5818±0.0034
c_4	0.08829±0.00188	−0.10766±0.00177	−0.2888±0.0176	20.4±2.4	−1.487±0.033
c_5	0.1543±0.0051	0.8167±0.0060			
c_6	−0.841±0.035	−0.4645±0.029			
c_7	0.0278±0.121				
c_8	7.77±0.25				
k_e/N m^{-1}	516.33142±0.00034	142.330545±0.000029	108.687296±0.000160	85.1648±0.0033	79.465512±0.000181
R_e/10^{-10} m	1.27460364±0.00000109	2.02068674±0.00000136	2.3608044±0.0000020	2.666665±0.0000034	2.78672481±0.00000173
$U_{1,0}$/m^{-1} u$^{1/2}$	296032.241±0.040	155426.0426±0.0130	135820.125±0.091	120227.8±2.3	116135.306±0.132
$U_{0,1}$/m^{-1} u	1037.63890±0.00020	412.85597±0.00023	302.465985±0.000047	237.06077±0.00053	217.074482±0.000026
t_0^{M}[c)]	[0.45673]	[0.825904]	[0.81]	[0.784]	[0.657]
t_1^{M}	−0.5713±0.0070	1.570±0.058			
t_2^{M}	−1.530±0.021				
t_0^{Cl}[c)]	[0.09966]	[−0.634116]	[−0.77]	[−0.815]	[−0.909]
t_1^{Cl}	−0.754±0.182				
u_1^{M}/10^6 m^{-1}	−6.12455±0.00202	−7.477±0.094			
u_2^{M}/10^6 m^{-1}	18.4086±0.0071				
u_3^{M}/10^6 m^{-1}	−15.225±0.185				
u_4^{M}/10^6 m^{-1}	23.22±0.84				
u_1^{Cl}/10^6 m^{-1}	−4.83±0.26				
u_2^{Cl}/10^6 m^{-1}	23.22±0.84				
σ[d)]	1.384	1.179	0.921	6.83	0.993
F[e)]	1.2 × 10^{16}	8.4 × 10^{14}	2.0 × 10^{13}	1.8 × 10^{11}	3.8 × 10^{13}

a) Each stated uncertainty corresponds to a single estimated standard error; uncertainties of k_e and R_e include errors associated with h and N_A. b) number of data in microwave and infrared regions respectively. c) [ ] indicates a value constrained during fit of spectral data. d) σ denotes normalised standard deviation. e) F denotes a statistic of which a maximal value conforms to a criterion of best model to fit available data.

to $J'' = 159$, likewise for bands 5–3, 6–4 and 7–5 for which heads are calculated to occur at $J'' = 92$, 92, and 91 respectively. For band 4–2 of $^{85}\mathrm{Rb}^{37}\mathrm{Cl}$ we assigned lines near the head at $J'' = 95$, from $J'' = 60$ below that value to $J'' = 123$ above, likewise for band 5–3 about its head at $J'' = 94$ and for band 8–6 about its head at $J'' = 93$. For $^{87}\mathrm{Rb}^{35}\mathrm{Cl}$ heads of bands 6–4 at $J'' = 92$ and 7–5 at $J'' = 92$ fall within regions in which our laser diodes can be tuned. The wave numbers of these heads are sensitive to values of rotational and vibrational parameters; the fact that we reproduce accurately these characteristic features with our fitted parameters, though numbering only six, confirms the accuracy of our assignments and the values of parameters deduced therefrom. All six primary parameters — $U_{1,0}$, $U_{0,1}$, c_1—c_4 — are statistically well defined, and secondary parameters k_e and R_e have relative estimated standard errors about 10^{-6}, including uncertainties of fundamental physical constants N_A and h involved in their evaluation from primary parameters.

Values of fixed and fitted coefficients, and related parameters, and presented in Table 2, for comparison with analogous parameters for HCl, LiCl, NaCl, and KCl similarly evaluated from global fits of available spectral data of these molecular species. Data of HCl are those of a previous analysis,[11] with new data[14—17] replacing obsolescent data of inferior quality covering the same range of v and J. Data of LiCl are those in a previous analysis,[18] whereas data of NaCl[19] in a previous analysis[20] were supplemented with additional spectral lines not otherwise duplicated.[21] Data of KCl are those used reported in a separate analysis[20] supplemented with further microwave data.[22] Parameters c_0, R_e, and equilibrium force coefficient k_e are evaluated from parameters $U_{1,0}$ and $U_{0,1}$ that are directly fitted. Notation of these and other parameters appearing in this table is explained in detail elsewhere;[11,12,23] in the latter paper[23] appears a similar table with values of corresponding parameters for fluorides of elements in group 13 of the periodic chart.

Comparison of values of significant parameters of five polar chloride molecules in Table 2 shows expected trends with increasing atomic number of element M in compound MCl. For instance, magnitudes of equilibrium internuclear distance R_e and of coefficient c_1, that influences primarily the shape of function $V(z)$ for potential energy, increase monotonically with molecular mass, whereas equilibrium force coefficient k_e decreases in the same order. Available data[19] from vibration-rotational spectra of KCl are fewer and have quality poorer than those of NaCl measured in the same laboratory; for this reason parameters deduced from these data are less reliable than those of other molecular species in Table 2, and apparent anomalies of parameters c_2, c_3, and c_4 with respect to periodic trends likely result from this condition. One can compare results in Table 2 with corresponding parameters of another chloride AlCl,[24] for which many and precise spectral data exist.

JFO thanks Japan Society for the Promotion of Science for a visiting fellowship at Josai University in 1998 October during which period spectral measurements were conducted and analysis was begun.

References

1 J. W. Trischka and R. Braunstein, *Phys. Rev.*, **96**, 968 (1954).

2 P. L. Clouser and W. Gordy, *Phys. Rev. A*, **A134**, 863 (1964).

3 S. A. Rice and W. Klemperer, *J. Chem. Phys.*, **27**, 573 (1957).

4 A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Story, and K. Street, *J. Chem. Phys.*, **48**, 2824 (1968).

5 F. Mehran, R. A. Brooks, and N. F. Ramsey, *Phys. Rev.*, **141**, 93 (1966).

6 R. R. Freeman, D. W. Johnson, and N. F. Ramsey, *J. Chem. Phys.*, **61**, 3471 (1974).

7 H. Uehara, K. Horiai, Y. Ozaki, and T. Konno, *Spectrochim. Acta, Part A*, **A50**, 389 (1994).

8 H. Uehara, K. Horiai, Y. Ozaki, and T. Konno, *J. Mol. Struct.*, **352/353**, 395 (1995).

9 H. Uehara, K. Horiai, Y. Ozaki, and T. Konno, *Chem. Phys. Lett.*, **215**, 505 (1993).

10 H. Uehara, T. Konno, Y. Ozaki, K. Horiai, K. Nakagawa, and J. W. C. Johns, *Can. J. Phys.*, **72**, 1145 (1994).

11 J. F. Ogilvie, *J. Phys., B*, **B27**, 47 (1994).

12 J. F. Ogilvie, "The Vibrational and Rotational Spectrometry of Diatomic Molecules," Academic Press, London, U.K. (1998).

13 J. F. Ogilvie, J. Oddershede, and S. P. A. Sauer, *Adv. Chem. Phys.*, **111**, 486 (1999).

14 P. De Natale, L. Lorini, M. Inguscio, G. Di Lonardo, and L. Fusina, *Chem. Phys. Lett.*, **273**, 253 (1997).

15 F. Lewen, E. Michael, R. Gendriesh, J. Stutzki, and G. Winnewisser, *J. Mol. Spectrosc.*, **183**, 207 (1997).

16 T. Klaus, S. P. Belov, and G. Winnewisser, *J. Mol. Spectrosc.*, **187**, 109 (1998).

17 T. Parekunnel, T. Hirao, R. J. LeRoy, and P. F. Bernath, *J. Mol. Spectrosc.*, **195**, 185 (1999).

18 J. F. Ogilvie, *Spectrosc. Lett.*, **25**, 1341 (1992).

19 R. S. Ram, M. Dulick, B. Guo, K. Q. Zhang, and P. F. Bernath, *J. Mol. Spectrosc.*, **183**, 360 (1997).

20 J. F. Ogilvie and M. Molski, *Spectrochim. Acta, Part A*, **A55**, 1427 (1999).

21 H. Uehara, K. Horiai, K. Nakagawa, and T. Fujimoto, *J. Mol. Spectrosc.*, **134**, 98 (1989).

22 C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, *Phys. Rev.*, **91**, 1395 (1953).

23 J. F. Ogilvie, H. Uehara, and K. Horiai, *J. Chem. Soc., Faraday Trans.*, **91**, 3007 (1995).

24 J. F. Ogilvie and S. C. Liao, *Acta Phys. Hung.*, **74**, 365 (1994).