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Fourier Transform Infrared Emission Spectroscopy of the $C^4\Delta$–$X^4\Phi$ System of ZrCl

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The high-resolution spectrum of ZrCl has been investigated in emission in the region 3000–10 000 cm^{-1} using a Fourier transform spectrometer. The bands were excited in a microwave discharge through a flowing mixture of $ZrCl_4$ and helium. New ZrCl bands observed in the interval 3600–4400 cm^{-1} have been assigned to a new $C^4\Delta$–$X^4\Phi$ electronic transition. Four bands with *R* heads at 4305.7, 4208.0, 4064.7, and 3897.4 cm^{-1} have been assigned as the 0–0 bands of the $^4\Delta_{1/2}$–$^4\Phi_{3/2}$, $^4\Delta_{3/2}$–$^4\Phi_{5/2}$, $^4\Delta_{5/2}$–$^4\Phi_{7/2}$, and $^4\Delta_{7/2}$–$^4\Phi_{9/2}$ subbands. A rotational analysis of the 0–0, 1–1, and 2–2 vibrational bands of the four subbands has been obtained and molecular constants have been extracted. Although there is no proof that the lower $^4\Phi$ state is the ground state of ZrCl, we have labeled this transition as $C^4\Delta$–$X^4\Phi$, consistent with the corresponding near-infrared transition of TiCl (R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.*, in press).

INTRODUCTION

The emission spectrum of ZrCl was initially observed by Carroll and Daly (*1*) from the radiofrequency excitation of $ZrCl_4$ vapor obtained by heating an anhydrous sample of $ZrCl_4$ powder. Many complex bands were observed in the region 280–420 nm which were tentatively classified into three electronic transitions named as system A (280–290 nm), system B (360–380 nm), and system C (400–415 nm). A tentative electronic assignment of $^4\Pi$–$^4\Sigma^-$ was suggested for system C on the basis of a vibrational analysis, although no rotational analysis was presented. The emission spectrum of ZrCl has also been recently studied by Jordan *et al.* (*2*), who excited the molecule in a low-temperature corona-excited supersonic jet discharge. They classified the bands in the region 400–415 nm into four groups of double-headed bands assigned as the $^4\Pi_{-1/2}$–$^4\Sigma^-$, $^4\Pi_{1/2}$–$^4\Sigma^-$, $^4\Pi_{3/2}$–$^4\Sigma^-$, and $^4\Pi_{5/2}$–$^4\Sigma^-$ subbands of a Hund's case (*a*) $^4\Pi$–Hund's case (*b*) $^4\Sigma^-$ transition. Again no rotational analysis of the bands was provided to support their assignments. Another transition of ZrCl has been observed in the near infrared by Phillips *et al.* (*3*), who reported a rotational analysis of numerous bands and concluded that these bands were probably due to a $^2\Pi$–$^2\Pi$ transition (although $^2\Delta$–$^2\Delta$ and $^2\Phi$–$^2\Phi$ assignments were not excluded). A definite assignment of the ground electronic state of ZrCl is still lacking. Sivaji and Rao have found violet and near-ultraviolet bands of ZrBr (*4*) and ZrI (*5*), similar to the Carroll and Daly systems of ZrCl (*1*).

There are no theoretical calculations for any of the Zr-containing halides to assist in the assignment of the observed spectra. However, an ab initio calculation for TiF has recently been carried out by Harrison (*6*) and some work is in progress at the University of Utah (*7*). The work of the Harrison group predicts a $^4\Phi$ ground state for TiF and also provides spectroscopic properties for several low-lying electronic states (*6*). Our recent observation of the $G^4\Phi$–$X^4\Phi$ transition of TiF near 15 000 cm^{-1} (*8*) is consistent with a $^4\Phi$ ground state. Recently we have also investigated the electronic spectra of TiCl in the region 3000–12 500 cm^{-1} (*9*) and have found three new electronic transitions which have been named $C^4\Delta$–$X^4\Phi$, $G^4\Phi$–$X^4\Phi$, and $G^4\Phi$–$C^4\Delta$. We have based our letter notation for the different electronic states of TiCl on the theoretical predictions for TiF (*6*) and the data available for the isovalent TiH (*10–12*).

In the present work we report on the results of a search for the electronic transitions of ZrCl in the region 3000–10 000 cm^{-1}. We have observed a $^4\Delta$–$^4\Phi$ electronic transition of ZrCl in the region 3700–4400 cm^{-1} which is analogous to the $C^4\Delta$–$X^4\Phi$ transition of TiCl (*9*). A rotational analysis of a number of vibrational bands of different subbands has been obtained and the spectroscopic data for all four spin components of the $X^4\Phi$ and $C^4\Delta$ states have been extracted. Several weaker bands and some complex bands remain to be assigned. Although we do not have any proof for our assignment of the lower state as the ground state, we have decided to maintain

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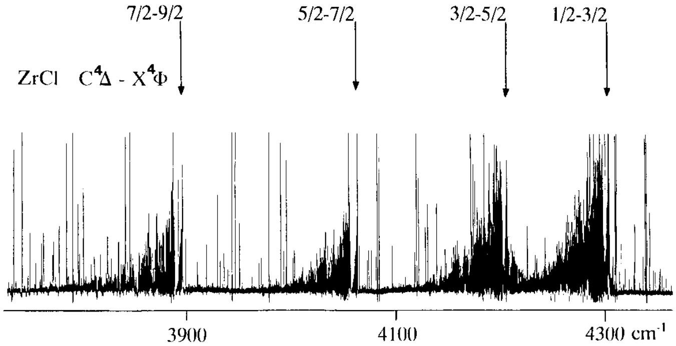

FIG. 1. A compressed portion of the $C^4\Delta - X^4\Phi$ transition of ZrCl with the *R* heads marked for the 0–0 vibrational bands of each subband.

the $C^4\Delta - X^4\Phi$ notation for this transition of ZrCl to be consistent with the recent results on the isovalent TiCl molecule.

EXPERIMENTAL DETAILS

The ZrCl molecules were excited in an electrodeless microwave discharge through a flowing mixture of 3 Torr of He and a trace of $ZrCl_4$. The discharge tube was made of quartz and had an outer diameter of 12 mm. A small glass bulb was attached to the discharge tube with a $\frac{1}{2}$-in. Cajon Ultratorr fitting. A small quantity of solid $ZrCl_4$ was placed in the bulb, which was constantly heated with a heat gun to maintain a blue-white discharge. The He gas flowed over the heated $ZrCl_4$ sample and carried the vapor into the discharge region. The emission from the discharge tube passed directly through the 8-mm entrance aperture of the 1-m Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. The spectra in the interval 1800–9000 cm^{-1} were initially recorded in the first-order alias using liquid nitrogen-cooled InSb detectors and Si filters. A total of 10 scans were coadded in about 60 min of integration at a resolution of 0.02 cm^{-1}. The region 3000–5000 cm^{-1} was also recorded in the third-order alias at a resolution of 0.01 cm^{-1}. We have used this spectrum in the analysis of the $C^4\Delta - X^4\Phi$ transition.

The spectral line positions were determined using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt lineshape function to each line. The spectra were calibrated using the wavenumbers of the vibration–rotation lines of the 1–0 band of HCl (*13*) which also appeared in emission in the same spectrum. The molecular lines of ZrCl had a typical width of 0.015 cm^{-1} and appeared with a maximum signal-to-noise ratio of 15:1 so that the best line positions are expected to be accurate to about ± 0.002 cm^{-1}.

OBSERVATION AND ANALYSIS

The present spectrum contains a number of new ZrCl bands in the region 3000–10 000 cm^{-1}. Several of the new bands observed in the interval 6000–10 000 cm^{-1} belong to the two subbands ($^2\Pi_{1/2} - {}^2\Pi_{1/2}$ and $^2\Pi_{3/2} - {}^2\Pi_{3/2}$) previously studied by Phillips *et al.* (*3*). In the region 3000–4500 cm^{-1}, however, there are four prominent groups of $|\Delta\Omega| = 1$ bands with strong *R* heads at 4305.7, 4208.0, 4064.7, and 3897.4 cm^{-1} which have been assigned as the 0–0 bands of the $^4\Delta_{1/2} - {}^4\Phi_{3/2}$, $^4\Delta_{3/2} - {}^4\Phi_{5/2}$, $^4\Delta_{5/2} - {}^4\Phi_{7/2}$, and $^4\Delta_{7/2} - {}^4\Phi_{9/2}$ subbands, respectively, of the $C^4\Delta - X^4\Phi$ transition. This assignment is consistent with our recent work on the analogous transition of TiCl in the region 3100–3400 cm^{-1}. A portion of the compressed spectrum of the $C^4\Delta - X^4\Phi$ transition of ZrCl is presented in Fig. 1. Each of the 0–0 bands in Fig. 1 is followed to lower wavenumbers by the 1–1, 2–2, and 3–3 bands with decreasing intensity. Off-diagonal bands were not identified in our spectra because of their very weak intensity; the vibrational intervals remain to be determined.

The rotational structure of each band consists of *P*, *Q*, and *R* branches. The *Q* branch is the strongest and the *P* branch is stronger than the *R* branch, consistent with a $\Delta\Omega = -1$ transition. The lines of the $^4\Delta_{1/2} - {}^4\Phi_{3/2}$ subband are doubled by the presence of appreciable Ω-doubling in the excited $^4\Delta_{1/2}$ state. The lines of the $^4\Delta_{3/2} - {}^4\Phi_{5/2}$, $^4\Delta_{5/2} - {}^4\Phi_{7/2}$, and $^4\Delta_{7/2} - {}^4\Phi_{9/2}$ subbands, however, do not show any Ω-doubling. Zr has five isotopes, ^{90}Zr (51.5%), ^{91}Z (11.2%), ^{92}Zr (17.2%), ^{94}Zr (17.4%), and ^{96}Zr (2.7%), but we have determined the molecular constants only for the most abundant $^{90}Zr^{35}Cl$ isotopomer. Some weak lines of the minor isotopomer $^{90}Zr^{37}Cl$ have also been observed for the strong bands but the data were not sufficient for an independent rotational analysis. A band with weak doubled *R* heads at 4309.3 and 4309.6 cm^{-1} was also found near the 0–0 band of the $^4\Delta_{1/2} - {}^4\Phi_{3/2}$ subband, but it probably belongs to another transition. Similarly, some rotational structure without any prominent head has been observed on the high wavenumber

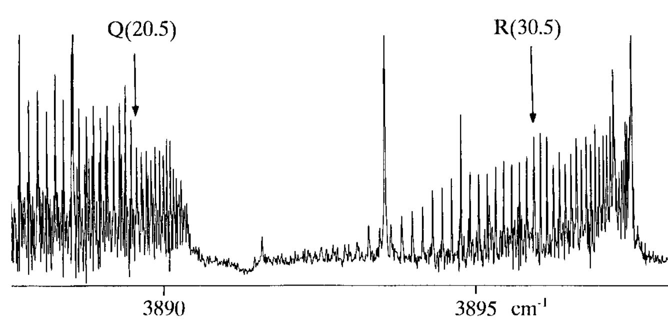

FIG. 2. An expanded portion of the 0–0 band of the $C^4\Delta_{7/2} - X^4\Phi_{9/2}$ subband of ZrCl near the *R* head.

TABLE 1
Observed Line Positions (in cm^{-1}) for the $C^4\Delta - X^4\Phi$ Transition of ZrCl

J	R_{ee}	O-C	P_{ee}	O-C	R_{ff}	O-C	P_{ff}	O-C	Q_{ef}	O-C	Q_{fe}	O-C	J
						$C^4\Delta_{1/2}$ - $X^4\Phi_{3/2}$ 0-0							
2.5									4300.345	5			2.5
3.5									4300.317	4			3.5
4.5									4300.286	6	4300.345	5	4.5
5.5							4299.022	2	4300.248	7	4300.317	3	5.5
6.5							4298.760	7	4300.202	5	4300.286	4	6.5
7.5							4298.484	4	4300.153	6	4300.248	5	7.5
8.5							4298.210	8	4300.094	4	4300.202	3	8.5
9.5							4297.920	2	4300.032	3	4300.153	4	9.5
10.5	4302.648	-1					4297.629	2	4299.965	4	4300.094	1	10.5
11.5	4302.812	3					4297.334	3	4299.889	3	4300.032	0	11.5
12.5	4302.959	-5			4303.135	3	4297.030	1	4299.811	4	4299.965	1	12.5
13.5	4303.109	-3	4296.564	-1	4303.296	3	4296.722	0	4299.723	1	4299.889	-1	13.5
14.5	4303.255	-1	4296.241	0	4303.453	5	4296.406	-3	4299.634	3	4299.811	-1	14.5
15.5	4303.391	-2	4295.908	-1			4296.093	3	4299.537	2	4299.723	-3	15.5
16.5	4303.524	-1	4295.574	1	4303.745	3	4295.764	-1	4299.437	5	4299.634	-2	16.5
17.5	4303.653	2		0	4303.882	2	4295.439	4	4299.328	4	4299.537	-4	17.5
18.5	4303.774	2	4294.877	-7	4304.012	0	4295.103	3	4299.213	2	4299.437	-2	18.5
19.5	4303.882	-6	4294.530	0	4304.140	1	4294.751	-8	4299.095	3	4299.328	-4	19.5
20.5	4303.994	-4	4294.170	-2	4304.261	0	4294.413	1	4298.969	1	4299.213	-6	20.5
21.5	4304.105	3	4293.804	-4	4304.375	-1	4294.058	-2	4298.840	2	4299.095	-6	21.5
22.5	4304.198	-3	4293.431	-8	4304.489	2	4293.713	10	4298.693	-10			22.5
23.5	4304.287	-6	4293.060	-5	4304.589	-3	4293.341	1	4298.554	-9			23.5
24.5	4304.375	-7	4292.678	-7	4304.685	-7	4292.973	1	4298.412	-5	4298.713	-2	24.5
25.5	4304.464	0	4292.295	-5	4304.794	8	4292.597	-1	4298.259	-6	4298.573	-2	25.5
26.5	4304.541	-2	4291.906	-4	4304.872	-3	4292.218	-2	4298.104	-5	4298.429	-1	26.5
27.5	4304.610	-5	4291.515	1	4304.957	-2	4291.834	-2	4297.943	-5	4298.278	-2	27.5
28.5	4304.685	3	4291.112	-2	4305.042	5	4291.446	-1	4297.777	-4	4298.124	-1	28.5
29.5	4304.739	-6	4290.706	-3	4305.108	-3	4291.049	-4	4297.604	-6	4297.964	-1	29.5
30.5	4304.794	-7	4290.293	-6	4305.180	0	4290.652	-3	4297.427	-6	4297.800	0	30.5
31.5	4304.849	-5	4289.879	-5	4305.244	1	4290.250	-1	4297.248	-4	4297.629	-1	31.5
32.5	4304.897	-3	4289.462	-1	4305.301	0	4289.840	-1	4297.063	-2	4297.454	0	32.5
33.5			4289.031	-7	4305.353	-2	4289.434	6	4296.868	-6	4297.274	-1	33.5
34.5	4304.982	2	4288.606	-3	4305.403	0	4289.007	-3	4296.675	-3	4297.087	-3	34.5
35.5	4305.015	2	4288.165	-10	4305.446	-1	4288.585	-1	4296.477	0	4296.897	-3	35.5
36.5	4305.042	1			4305.486	0	4288.165	7	4296.270	-2	4296.704	-2	36.5
37.5	4305.067	3	4287.288	-4	4305.516	-3			4296.059	-3	4296.503	-3	37.5
38.5	4305.084	2	4286.844	1	4305.549	0	4287.288	0	4295.842	-4	4296.302	0	38.5
39.5			4286.397	6	4305.570	-3	4286.844	-2	4295.624	-2	4296.093	0	39.5
40.5			4285.930	-3	4305.597	4	4286.397	-3	4295.401	-1	4295.881	1	40.5
41.5			4285.470	-2			4285.953	5	4295.173	0	4295.665	3	41.5
42.5			4285.005	0			4285.498	5	4294.940	-1	4295.439	0	42.5
43.5			4284.538	4			4285.029	-3	4294.705	1	4295.215	3	43.5
44.5			4284.059	0			4284.571	3	4294.463	1	4294.983	2	44.5
45.5			4283.581	1			4284.105	6	4294.217	2	4294.751	5	45.5
46.5			4283.099	3			4283.628	2	4293.967	2	4294.507	3	46.5
47.5			4282.607	-1			4283.150	1	4293.713	4	4294.263	3	47.5
48.5			4282.118	2			4282.669	3	4293.454	4	4294.014	3	48.5
49.5			4281.622	2			4282.183	2	4293.190	3	4293.762	5	49.5
50.5			4281.118	-1			4281.692	2	4292.922	4	4293.503	3	50.5
51.5	4304.920	8	4280.614	0			4281.196	1	4292.650	4	4293.238	1	51.5
52.5	4304.872	5	4280.108	3			4280.700	4	4292.373	3	4292.973	2	52.5
53.5	4304.822	3	4279.601	9			4280.196	3	4292.094	4	4292.703	3	53.5
54.5	4304.768	1	4279.075	1			4279.690	4	4291.809	4	4292.426	1	54.5
55.5	4304.715	5	4278.555	1			4279.179	5	4291.515	0	4292.149	3	55.5
56.5	4304.654	4	4278.032	4			4278.659	1	4291.226	3	4291.860	-2	56.5
57.5	4304.589	4	4277.501	3			4278.137	-1	4290.929	4	4291.578	3	57.5
58.5	4304.515	1	4276.971	6			4277.616	3	4290.625	1	4291.284	2	58.5
59.5	4304.441	0	4276.423	-4			4277.087	2	4290.319	1	4290.988	2	59.5
60.5			4275.886	1			4276.552	-1	4290.011	3	4290.684	-1	60.5
61.5			4275.340	2			4276.015	0	4289.695	2	4290.381	1	61.5
62.5			4274.789	1			4275.475	1	4289.376	0	4290.070	0	62.5
63.5			4274.233	-1			4274.928	-2	4289.053	0	4289.756	-1	63.5
64.5	4304.012	3	4273.677	1			4274.379	0	4288.725	-1	4289.434	-5	64.5
65.5	4303.909	0	4273.111	-2	4304.633	-6	4273.825	0	4288.396	1	4289.116	0	65.5
66.5	4303.807	2	4272.542	-4	4304.541	-2	4273.263	-5	4288.060	0	4288.788	-2	66.5
67.5	4303.698	1	4271.972	-3	4304.441	-2	4272.705	0			4288.456	-2	67.5
68.5	4303.585	1	4271.402	2	4304.336	-3	4272.135	-3	4287.375	-2	4288.120	-3	68.5
69.5	4303.470	3	4270.823	3	4304.229	-1	4271.564	-3	4287.027	-1	4287.779	-4	69.5
70.5	4303.343	-3	4270.236	-1	4304.105	-12	4270.993	1	4286.674	-2	4287.436	-3	70.5

Note. O-C are observed minus calculated line positions in the units of 10^{-3} cm^{-1} and asterisks mark perturbed lines.

TABLE 1—*Continued*

J	R_{ee}	O-C	P_{ee}	O-C	R_{ff}	O-C	P_{ff}	O-C	Q_{ef}	O-C	Q_{fe}	O-C	J
71.5	4303.219	-1	4269.647	-2	4303.994	-5	4270.404	-7	4286.317	-2	4287.086	-3	71.5
72.5	4303.084	-5	4269.053	-3			4269.821	-7	4285.953	-4	4286.732	-4	72.5
73.5	4302.959	4	4268.468	8			4269.233	-6	4285.592	0	4286.378	0	73.5
74.5	4302.812	-4	4267.856	-3	4303.616	-1	4268.639	-6	4285.221	-1	4286.011	-4	74.5
75.5	4302.670	-2	4267.254	1	4303.470	-10	4268.044	-4	4284.846	-1	4285.644	-5	75.5
76.5	4302.521	-2	4266.640	-5	4303.343	3	4267.442	-4	4284.465	-3	4285.278	1	76.5
77.5	4302.370	0	4266.029	-1	4303.192	-2	4266.839	0	4284.085	0	4284.897	-4	77.5
78.5	4302.215	2	4265.411	-1	4303.043	0	4266.225	-4	4283.696	-1	4284.520	-1	78.5
79.5	4302.048	-3	4264.786	-3	4302.886	-2	4265.612	0	4283.303	-2	4284.133	-3	79.5
80.5	4301.891	7	4264.163	1	4302.729	0	4264.984	-9	4282.907	-1	4283.743	-2	80.5
81.5	4301.716	3	4263.531	0	4302.564	1	4264.363	-5	4282.506	-1	4283.350	-1	81.5
82.5	4301.541	4	4262.899	3	4302.394	0	4263.743	4	4282.099	-2	4282.952	0	82.5
83.5	4301.359	2	4262.257	2	4302.215	-6	4263.107	1	4281.692	1	4282.550	2	83.5
84.5	4301.174	2	4261.613	2	4302.048	6	4262.473	4	4281.278	1	4282.143	3	84.5
85.5	4300.987	4	4260.965	2	4301.861	3	4261.831	5	4280.861	4	4281.733	5	85.5
86.5	4300.797	8	4260.314	4	4301.673	2	4261.181	2	4280.439	5	4281.313	3	86.5
87.5	4300.591	-1	4259.655	2	4301.487	8	4260.530	1	4280.014	7	4280.890	0	87.5
88.5	4300.381	-8	4258.992	0	4301.290	8	4259.880	7			4280.467	4	88.5
89.5	4300.179	-3	4258.325	-2	4301.083	2	4259.220	6			4280.038	5	89.5
90.5	4299.965	-6	4257.656	-1	4300.881	6	4258.557	6					90.5
91.5	4299.753	-3	4256.988	4	4300.672	7	4257.887	3					91.5
92.5			4256.300	-8	4300.452	0	4257.211	-1					92.5
93.5			4255.619	-9	4300.227	-7	4256.534	-3					93.5
94.5			4254.935	-10	4300.005	-7							94.5
95.5					4299.782	-5							95.5
$C^4\Delta_{1/2}$ - $X^4\Phi_{3/2}$ 1-1													
6.5			4278.530	1									6.5
7.5			4278.251	0	4282.054	6							7.5
8.5			4277.975	6	4282.228	-11			4279.947	0	4280.014	-6	8.5
9.5	4282.333	-5	4277.669	-11	4282.416	-10			4279.897	5	4279.971	-1	9.5
10.5	4282.506	-3	4277.386	0	4282.607	1			4279.843	12	4279.922	3	10.5
11.5	4282.669	-8	4277.087	1	4282.780	-1			4279.773	8			11.5
12.5	4282.836	-2	4276.786	4	4282.952	2	4276.883	5	4279.690	-4	4279.797	-1	12.5
13.5	4282.996	1	4276.470	-2	4283.099	-16	4276.575	-1	4279.623	6	4279.731	3	13.5
14.5	4283.150	4	4276.157	0			4276.266	-3	4279.544	9	4279.657	2	14.5
15.5	4283.303	11	4275.827	-9	4283.426	-2	4275.960	4	4279.448	0	4279.576	1	15.5
16.5			4275.510	0	4283.581	5	4275.641	3	4279.354	-1	4279.490	0	16.5
17.5	4283.581	14	4275.179	1			4275.317	3	4279.259	3	4279.401	1	17.5
18.5	4283.696	0	4274.839	-3	4283.851	-5	4274.988	2			4279.306	2	18.5
19.5	4283.822	2	4274.503	2	4283.984	-4	4274.650	-2	4279.049	5	4279.206	2	19.5
20.5	4283.941	1	4274.162	9	4284.105	-10	4274.312	-1	4278.928	-2	4279.100	3	20.5
21.5	4284.059	5	4273.803	2	4284.231	-6	4273.972	3	4278.813	2	4278.990	4	21.5
22.5	4284.156	-6	4273.441	-3	4284.350	-3	4273.617	-3	4278.685	-1	4278.875	5	22.5
23.5	4284.260	-5	4273.081	0	4284.461	-3	4273.263	-2	4278.555	-2	4278.746	-2	23.5
24.5	4284.361	-2	4272.705	-8			4272.902	-3	4278.422	1	4278.620	-1	24.5
25.5			4272.333	-7	4284.666	-4	4272.542	3	4278.279	-2	4278.490	1	25.5
26.5	4284.538	-5			4284.763	-2	4272.160	-9	4278.137	1	4278.350	0	26.5
27.5	4284.618	-7	4271.579	1	4284.846	-10	4271.793	0	4277.979	-6	4278.210	2	27.5
28.5			4271.184	-5	4284.943	2	4271.402	-10	4277.833	3	4278.057	-3	28.5
29.5	4284.763	-11	4270.797	1			4271.024	-2	4277.669	0	4277.908	1	29.5
30.5	4284.846	5	4270.404	7	4285.093	-1	4270.637	2	4277.501	-1	4277.748	0	30.5
31.5	4284.898	-4	4269.993	-1	4285.165	2	4270.236	-3	4277.329	-2	4277.588	2	31.5
32.5	4284.966	8	4269.583	-2			4269.843	5	4277.155	0	4277.416	0	32.5
33.5	4285.007	-3	4269.166	-4	4285.276	-11	4269.436	4	4276.971	-3	4277.251	8	33.5
34.5	4285.068	12	4268.756	5	4285.343	3	4269.025	4	4276.786	-2	4277.064	0	34.5
35.5	4285.093	-3	4268.329	2	4285.398	9	4268.616	11	4276.596	0	4276.883	2	35.5
36.5	4285.139	7	4267.897	-2	4285.439	7	4268.185	2	4276.397	-3	4276.693	1	36.5
37.5	4285.166	2	4267.466	1	4285.471	0	4267.758	0	4276.196	-2	4276.497	-1	37.5
38.5	4285.190	0	4267.023	-3	4285.507	3	4267.324	-2	4275.991	-1	4276.300	1	38.5
39.5			4266.585	2	4285.537	5	4266.883	-7	4275.779	-1	4276.094	-1	39.5
40.5			4266.135	1	4285.560	4	4266.450	1	4275.565	1	4275.886	0	40.5
41.5			4265.686	6			4266.005	2	4275.340	-2	4275.672	0	41.5
42.5			4265.219	-3			4265.551	0	4275.115	0	4275.452	-1	42.5
43.5			4264.764	6			4265.097	1	4274.890	5	4275.230	0	43.5
44.5			4264.293	3			4264.639	4	4274.650	2	4275.014	13	44.5

TABLE 1—*Continued*

J	R_{ee}	O-C	P_{ee}	O-C	R_{ff}	O-C	P_{ff}	O-C	Q_{ef}	O-C	Q_{fe}	O-C	J
45.5			4263.821	4			4264.163	-7	4274.406	-2	4274.766	-2	45.5
46.5			4263.344	4			4263.699	0	4274.162	0	4274.529	-1	46.5
47.5			4262.858	1			4263.228	4	4273.910	-1	4274.284	-2	47.5
48.5			4262.370	1			4262.745	0	4273.655	-1	4274.040	2	48.5
49.5			4261.879	1			4262.257	-3	4273.397	1	4273.784	-1	49.5
50.5			4261.382	1			4261.770	-1	4273.128	-2	4273.531	4	50.5
51.5			4260.877	-2			4261.275	-2	4272.861	1	4273.263	-2	51.5
52.5			4260.370	-3			4260.774	-4	4272.582	-3	4272.993	-4	52.5
53.5			4259.862	0			4260.268	-6	4272.304	-2	4272.721	-4	53.5
54.5			4259.342	-5			4259.759	-7	4272.017	-5	4272.442	-6	54.5
55.5			4258.820	-6			4259.248	-4	4271.726	-7	4272.160	-7	55.5
56.5			4258.298	-3			4258.728	-7	4271.432	-7	4271.870	-10	56.5
57.5			4257.764	-8			4258.209	-4	4271.132	-9	4271.579	-10	57.5
58.5			4257.228*	-10			4257.675*	-10	4270.823*	-15	4271.279*	-13	58.5
59.5			4256.688*	-11			4257.139*	-15	4270.517*	-13	4270.978*	-14	59.5
60.5			4256.138*	-17			4256.593*	-24	4270.201*	-17	4270.666*	-21	60.5
61.5			4255.587*	-20			4256.052*	-25	4269.876*	-24	4270.350*	-26	61.5
62.5			4255.022*	-33			4255.503*	-28	4269.546*	-33	4270.026*	-36	62.5
63.5			4254.462*	-36			4254.935*	-46	4269.208*	-44	4269.695*	-47	63.5
64.5			4253.879*	-57			4254.382*	-44	4268.858*	-63	4269.347*	-70	64.5
65.5							4253.813*	-53			4268.994*	-95	65.5
66.5							4253.235*	-67					66.5
67.5													67.5
68.5									4267.646*	96	4268.138*	65	68.5
69.5			4251.100*	42					4267.254*	59	4267.786*	60	69.5
70.5							4251.040*	40	4266.883*	47	4267.415*	41	70.5
71.5			4249.910*	35			4250.446*	33	4266.505*	33	4267.047*	31	71.5
72.5			4249.310*	33			4249.855*	34	4266.135*	31	4266.677*	23	72.5
73.5			4248.698*	24			4249.252*	27	4265.754*	24	4266.309*	21	73.5
74.5			4248.086*	19			4248.645*	22	4265.369*	17	4265.933*	16	74.5
75.5			4247.469*	16			4248.033*	15	4264.984*	15	4265.551*	11	75.5
76.5			4246.854*	18			4247.421*	13	4264.591*	9	4265.166*	7	76.5
77.5			4246.226	11			4246.797	5	4264.200	10	4264.765	-8	77.5
78.5			4245.596	7			4246.177	5	4263.798	5	4264.387	4	78.5
79.5			4244.964	7			4245.552	4	4263.395	4	4263.993	6	79.5
80.5							4244.919	1	4262.984	-1	4263.583	-3	80.5
81.5			4243.682	1			4244.283	0	4262.573	0	4263.179	-2	81.5
82.5			4243.036	0			4243.638	-7	4262.158	1	4262.769	-2	82.5
83.5			4242.388	1			4242.997	-3	4261.736	1	4262.352	-4	83.5
84.5			4241.730	-1			4242.351	-1	4261.308	0	4261.930	-6	84.5
85.5			4241.069	-2			4241.699	1	4260.877	0	4261.505	-5	85.5
86.5			4240.411	4			4241.033	-6	4260.438	-3	4261.076	-4	86.5
87.5			4239.732	-5			4240.371	-5	4259.996	-3	4260.642	-3	87.5
88.5			4239.060	-2			4239.704	-2			4260.206	1	88.5
89.5			4238.380	-3			4239.032	-2	4259.100	-2	4259.759	1	89.5
90.5			4237.695	-2			4238.354	-1	4258.638	-6	4259.308	1	90.5
91.5							4237.669	-1	4258.182	-1	4258.852	1	91.5
92.5							4236.988	8	4257.718	4	4258.396	7	92.5
93.5									4257.244	3			93.5

$C^4\Delta_{1/2} - X^4\Phi_{3/2}$ 2-2

J	R_{ee}	O-C	P_{ee}	O-C	R_{ff}	O-C	P_{ff}	O-C	Q_{ef}	O-C	Q_{fe}	O-C	J
8.5							4257.358	8	4259.278	9			8.5
9.5							4257.073	1	4259.220	2	4259.278	-2	9.5
10.5							4256.795	7	4259.163	4	4259.220	-10	10.5
11.5							4256.503	3	4259.100	3	4259.163	-9	11.5
12.5	4262.158	-3			4262.257	8	4256.207	1	4259.037	8	4259.100	-11	12.5
13.5	4262.328	9	4255.814	-10	4262.417	3	4255.904	-2			4259.037	-7	13.5
14.5	4262.473	-1	4255.503	-11	4262.573	-1			4258.875	-2			14.5
15.5											4258.896	1	15.5
16.5	4262.769	4	4254.878	1	4262.883	4	4254.979	0	4258.703	-3	4258.820	7	16.5
17.5	4262.899	-4	4254.549	-2			4254.658	-1	4258.613	2	4258.728	3	17.5
18.5					4263.160	-3	4254.335	1	4258.511	-2	4258.638	6	18.5
19.5	4263.160	-4	4253.879	-6	4263.290	-7	4254.002	-3	4258.409	0	4258.535	0	19.5
20.5	4263.290	3	4253.533	-10	4263.422	-4	4253.674	4	4258.298	-1	4258.434	2	20.5

TABLE 1—*Continued*

J	R_{ee}	O-C	P_{ee}	O-C	R_{ff}	O-C	P_{ff}	O-C	Q_{ef}	O-C	Q_{fe}	O-C	J
21.5									4258.182	-3	4258.325	1	21.5
22.5					4263.663	-6	4252.984	-1	4258.068	3	4258.209	-2	22.5
23.5	4263.632	8	4252.493	4	4263.772	-10	4252.635	0	4257.942	1	4258.099	6	23.5
24.5	4263.725	-1	4252.124	-3	4263.888	-3	4252.276	-3	4257.815	4	4257.970	1	24.5
25.5	4263.821	-2	4251.762	1	4263.993	-1	4251.917	-2	4257.675	-1	4257.842	1	25.5
26.5	4263.915	0	4251.384	-5	4264.089	-2			4257.538	2	4257.703	-3	26.5
27.5	4263.993	-8	4251.014	2			4251.178	-6	4257.393	2	4257.567	-1	27.5
28.5	4264.089	6	4250.632	1	4264.272	-1	4250.805	-3	4257.244	4	4257.425	1	28.5
29.5	4264.163	4	4250.247	4	4264.363	8	4250.424	-3	4257.091	5	4257.274	-1	29.5
30.5	4264.235	4	4249.855	3	4264.437	4	4250.039	-3	4256.926	0	4257.118	-3	30.5
31.5	4264.293	-3	4249.460	5	4264.509	4	4249.654	3	4256.762	2	4256.960	-2	31.5
32.5	4264.363	5	4249.050	-2			4249.252	-3	4256.593	4	4256.795	-3	32.5
33.5	4264.409	-4	4248.645	0	4264.639	4	4248.858	4	4256.417	3	4256.628	-1	33.5
34.5	4264.466	1	4248.239	5	4264.687	-5	4248.450	1	4256.233	-1	4256.456	1	34.5
35.5	4264.509	-1	4247.817	0	4264.741	-3	4248.033	-5	4256.052	4	4256.275	-1	35.5
36.5	4264.552	1	4247.396	1	4264.786	-5	4247.625	3	4255.856	-1	4256.093	2	36.5
37.5	4264.591	5	4246.968	0	4264.830	-3	4247.206	5	4255.661	0	4255.904	3	37.5
38.5	4264.615	-2	4246.537	1	4264.871	2	4246.771	-4	4255.457	-3	4255.705	-2	38.5
39.5	4264.639	-3	4246.098	0	4264.898	-3	4246.343	-1	4255.254	-1	4255.503	-5	39.5
40.5	4264.664	2	4245.666	9			4245.911	2	4255.044	1	4255.303	0	40.5
41.5	4264.687	10	4245.212	2	4264.942	-7	4245.466	-2	4254.827	-1	4255.091	-2	41.5
42.5			4244.757	0	4264.960	-6	4245.025	2	4254.607	0	4254.878	-1	42.5
43.5			4244.301	1			4244.574	1	4254.382	1	4254.658	-1	43.5
44.5			4243.838	-1			4244.116	-1	4254.152	1	4254.432	-3	44.5
45.5			4243.373	0			4243.657	0	4253.916	2	4254.202	-4	45.5
46.5			4242.902	2			4243.191	-1	4253.674	0	4253.971	1	46.5
47.5			4242.419	-5			4242.717	-4	4253.428	1	4253.729	-2	47.5
48.5			4241.942	-1			4242.246	0	4253.179	2	4253.484	-3	48.5
49.5			4241.457	1			4241.764	-1	4252.920	0	4253.235	-2	49.5
50.5			4240.962	-2			4241.279	-2	4252.659	-1	4252.984	1	50.5
51.5			4240.470	1			4240.788	-3	4252.399	5	4252.720	-3	51.5
52.5			4239.970	3			4240.300	4	4252.124	1	4252.457	-1	52.5
53.5			4239.464	2			4239.797	1	4251.849	1	4252.190	1	53.5
54.5			4238.953	3			4239.288	-4	4251.567	0	4251.917	3	54.5
55.5			4238.434	-1			4238.786	4	4251.282	0	4251.638	3	55.5
56.5			4237.912	-2			4238.267	-2	4250.991	0	4251.352	1	56.5
57.5			4237.393	4			4237.748	-1	4250.697	1	4251.067	5	57.5
58.5			4236.860	2			4237.220	-5	4250.398	3	4250.767	-1	58.5
59.5							4236.694	-2	4250.089	0	4250.471	1	59.5
60.5							4236.161	-1	4249.778	-1	4250.164	-1	60.5
61.5									4249.460	-4	4249.855	-2	61.5
62.5									4249.143	-1	4249.544	2	62.5
63.5									4248.820	0	4249.226	2	63.5
64.5									4248.489	0	4248.901	1	64.5
65.5									4248.153	-2	4248.570	-2	65.5
66.5									4247.817	2	4248.239	0	66.5
67.5									4247.469	-1	4247.905	4	67.5
68.5									4247.120	-2	4247.561	3	68.5
69.5									4246.771	4	4247.206	-3	69.5
70.5									4246.406	-2	4246.854	-3	70.5
71.5									4246.040	-4	4246.501	2	71.5
72.5									4245.666	-10	4246.143	6	72.5
73.5									4245.298	-5	4245.777	7	73.5
74.5									4244.919	-5	4245.402	4	74.5
75.5									4244.534	-7	4245.025	4	75.5
76.5									4244.148	-6	4244.647	7	76.5
77.5									4243.748	-13	4244.258	4	77.5
78.5											4243.865	2	78.5
79.5											4243.468	0	79.5

TABLE 1—*Continued*

J	R	O-C	P	O-C	Q	O-C	R	O-C	P	O-C	Q	O-C	J
		$^4\Delta_{3/2}$ - $^4\Phi_{5/2}$ 0-0							$^4\Delta_{3/2}$ - $^4\Phi_{5/2}$ 1-1				
8.5			4201.201	4	4203.190	0							8.5
9.5			4200.900	-7	4203.138	3			4183.907	7			9.5
10.5			4200.609	-3	4203.066	-9			4183.603	5			10.5
11.5	4205.931	-8	4200.304	-7	4202.997	-11	4188.892	1	4183.292	2			11.5
12.5	4206.092	-9			4202.930	-6	4189.046	2					12.5
13.5	4206.251	-6	4199.694	2	4202.851	-7	4189.191	1	4182.662	4	4185.808	1	13.5
14.5	4206.406	-2	4199.368	-6	4202.768	-5	4189.331	0	4182.334	2	4185.716	1	14.5
15.5	4206.548	-4	4199.047	-3	4202.680	-4	4189.464	-2	4182.000	0	4185.611	-5	15.5
16.5	4206.687	-4	4198.720	0	4202.592	4	4189.595	0	4181.668	6	4185.513	1	16.5
17.5	4206.822	-1	4198.387	3	4202.486	-1	4189.722	5	4181.312	-6	4185.401	0	17.5
18.5	4206.949	-1	4198.540	11	4202.382	3	4189.829	-5	4180.967	-3	4185.287	1	18.5
19.5	4207.073	3	4197.702	8	4202.270	5	4189.945	-1	4180.614	0	4185.159	-5	19.5
20.5	4207.187	3	4197.344	4	4202.150	5	4190.044	-8	4180.249	-5	4185.037	0	20.5
21.5	4207.299	7	4196.985	6	4202.021	3	4190.152	0	4179.886	-2	4184.905	1	21.5
22.5	4207.403	9	4196.620	8	4201.890	5	4190.247	0	4179.522	5	4184.765	-1	22.5
23.5	4207.492	4			4201.751	4	4190.335	-1	4179.135	-6	4184.620	-2	23.5
24.5	4207.576	0	4195.863	5	4201.604	4	4190.422	1	4178.759	0	4184.472	-2	24.5
25.5	4207.660	4	4195.476	5	4201.450	4	4190.502	2	4178.375	3	4184.319	0	25.5
26.5	4207.727	-3	4195.081	4	4201.289	2	4190.571	-3	4177.978	-2	4184.160	-1	26.5
27.5	4207.796	0	4194.678	3	4201.118	0	4190.654	11	4177.579	-4	4183.994	-3	27.5
28.5	4207.858	4	4194.266	2	4200.944	2					4183.825	-3	28.5
29.5	4207.903	-1	4193.847	0	4200.759	1	4190.767	1	4176.779	4	4183.654	-1	29.5
30.5	4207.947	2	4193.420	-1	4200.565	-1	4190.821	1	4176.362	-2	4183.474	-2	30.5
31.5	4207.975	-2	4192.984	-1	4200.364	-1	4190.870	0	4175.948	-1	4183.292	-1	31.5
32.5	4208.005	5	4192.539	-1	4200.151	-3	4190.914	-1			4183.104	-1	32.5
33.5			4192.082	-4	4199.927	-6	4190.957	1	4175.104	1	4182.912	-1	33.5
34.5			4191.617	-5	4199.694	-7	4190.991	0	4174.674	1	4182.716	0	34.5
35.5	4208.005	-1	4191.141	-4	4199.454	-5	4191.022	-1	4174.245	5	4182.515	0	35.5
36.5	4207.975	-11	4190.654	-4	4199.200	-5	4191.049	-2	4173.803	1	4182.306	-4	36.5
37.5	4207.947	-7	4190.152	-6	4198.934	-6	4191.075	2	4173.362	2	4182.102	1	37.5
38.5	4207.903	-4	4189.640	-5	4198.652	-7	4191.096	4	4172.915	1	4181.887	1	38.5
39.5	4207.842	-5	4189.114	-4	4198.362	-4	4191.118	12	4172.465	2	4181.668	0	39.5
40.5	4207.771	-1	4188.573	-4	4198.054	-4			4172.011	2	4181.448	2	40.5
41.5	4207.681	1	4188.016	-2	4197.730	-3			4171.551	1	4181.221	1	41.5
42.5	4207.576	4	4187.444	0	4197.390	-1			4171.090	3	4180.990	1	42.5
43.5	4207.448	4	4186.850	0	4197.032	1			4170.622	2	4180.757	2	43.5
44.5			4186.240	2	4196.653	2			4170.150	0	4180.519	2	44.5
45.5			4185.611	6	4196.255	4			4169.675	-1	4180.276	1	45.5
46.5			4184.955	6	4195.837	7			4169.196	-1	4180.027	0	46.5
47.5			4184.277	6	4195.388	5			4168.715	0	4179.777	0	47.5
48.5			4183.572	5	4194.918	6			4168.228	0	4179.522	-1	48.5
49.5			4182.842	6	4194.419	5			4167.737	-1	4179.263	-2	49.5
50.5					4193.890	4			4167.241	-2	4179.002	1	50.5
51.5			4181.285	0	4193.330	2			4166.746	1	4178.735	0	51.5
52.5			4180.459	-2	4192.735	-3			4166.245	2	4178.464	-1	52.5
53.5			4179.594	-8	4192.106	-5			4165.734	-3	4178.189	-1	53.5
54.5			4178.704	-3	4191.438	-10			4165.226	-1	4177.910	-1	54.5
55.5					4190.739	-5			4164.710	-2	4177.628	-1	55.5
56.5					4189.994	-5			4164.193	-1	4177.341	-1	56.5
57.5					4189.213	6			4163.669	-3	4177.049	-1	57.5
58.5									4163.145	0	4176.754	-2	58.5
59.5									4162.616	1	4176.455	-1	59.5
60.5									4162.079	-1	4176.152	-1	60.5
61.5									4161.546	4	4175.843	-2	61.5
62.5									4160.996	-2			62.5
63.5									4160.449	-3	4175.219	2	63.5
64.5									4159.905	5	4174.898	1	64.5
65.5									4159.344	-1	4174.574	2	65.5
66.5									4158.790	3	4174.245	1	66.5
67.5									4158.228	5	4173.915	3	67.5
68.5											4173.578	2	68.5
69.5											4173.236	0	69.5
70.5											4172.891	-1	70.5
71.5											4172.543	-2	71.5
72.5											4172.191	-3	72.5
73.5											4171.829	-11	73.5

TABLE 1—*Continued*

J	R	O-C	P	O-C	Q	O-C	R	O-C	P	O-C	Q	O-C	J
			$^4\Delta_{3/2}$ - $^4\Phi_{5/2}$ 2-2						$^4\Delta_{5/2}$ - $^4\Phi_{7/2}$ 0-0				
3.5											4057.988	5	3.5
4.5											4057.965	1	4.5
5.5			4160.477	1							4057.941	-1	5.5
6.5			4160.206	-6	4161.727	4					4057.915	0	6.5
7.5			4159.947	3	4161.683	-3	4059.884	3			4057.878	-6	7.5
8.5			4159.668	-2	4161.646	2	4060.083	2			4057.850	0	8.5
9.5	4164.035	-3	4159.391	-1	4161.599	1	4060.284	7			4057.815	4	9.5
10.5	4164.220	0	4159.112	3	4161.546	-2	4060.472	3			4057.769	1	10.5
11.5	4164.396	0	4158.819	-2	4161.495	3	4060.658	2			4057.723	2	11.5
12.5	4164.570	3	4158.535	7	4161.433	1	4060.842	3			4057.670	1	12.5
13.5	4164.735	1	4158.228	-2	4161.365	-1	4061.021	2	4054.443	-1	4057.614	0	13.5
14.5	4164.896	0	4157.919	-9	4161.295	-1	4061.195	1	4054.153	3	4057.554	0	14.5
15.5	4165.055	2	4157.619	-2	4161.223	2	4061.367	2	4053.849	-3	4057.490	-1	15.5
16.5	4165.202	-4	4157.308	-1	4161.140	-1	4061.534	2	4053.551	2	4057.422	-2	16.5
17.5	4165.353	-1	4156.991	-1	4161.056	0	4061.697	2	4053.244	1	4057.352	1	17.5
18.5	4165.498	2	4156.672	1	4160.968	1	4061.856	3	4052.933	1	4057.278	2	18.5
19.5	4165.635	2	4156.342	-2	4160.877	4	4062.011	3	4052.614	-4	4057.195	-1	19.5
20.5	4165.764	-2	4156.013	0	4160.776	2	4062.159	1	4052.301	2	4057.111	0	20.5
21.5	4165.894	-1	4155.676	-1	4160.668	-2	4062.304	0	4051.977	1	4057.024	1	21.5
22.5	4166.017	-1	4155.333	-4	4160.562	1	4062.448	1	4051.650	1	4056.933	2	22.5
23.5	4166.134	-2	4154.990	-1	4160.449	1	4062.585	1	4051.318	-1	4056.834	0	23.5
24.5	4166.245	-5	4154.641	1	4160.330	1	4062.718	0	4050.984	1	4056.732	-2	24.5
25.5	4166.361	2	4154.287	1	4160.206	0	4062.847	-1	4050.641	-3	4056.625	-3	25.5
26.5	4166.467	4	4153.927	1	4160.080	2	4062.972	-1	4050.300	0	4056.518	-2	26.5
27.5	4166.562	-1	4153.564	2	4159.947	0	4063.094	0	4049.953	0	4056.406	0	27.5
28.5	4166.656	-1	4153.193	0	4159.810	1	4063.211	-1	4049.600	-2	4056.287	-2	28.5
29.5	4166.746	0	4152.816	-3	4159.668	1	4063.323	-1	4049.245	-1	4056.166	-2	29.5
30.5	4166.830	-1	4152.442	2	4159.519	0	4063.432	-1	4048.885	-2	4056.041	-1	30.5
31.5	4166.910	-1	4152.057	1	4159.369	1	4063.536	-2	4048.521	-1	4055.912	-1	31.5
32.5	4166.987	1	4151.667	-1	4159.212	0	4063.639	1	4048.154	0	4055.778	-1	32.5
33.5	4167.058	1	4151.275	-1	4159.051	1	4063.732	-2	4047.781	-1	4055.640	-2	33.5
34.5	4167.122	0	4150.877	-1	4158.885	1	4063.824	-2	4047.403	-3	4055.497	-2	34.5
35.5			4150.474	-2	4158.714	0	4063.912	-2	4047.025	0	4055.351	-2	-0.5
36.5	4167.241	3	4150.069	1	4158.535	-4	4063.995	-2	4046.639	-2	4055.201	-1	36.5
37.5	4167.290	0	4149.659	2	4158.358	0	4064.076	-1	4046.252	-1	4055.046	-1	37.5
38.5	4167.334	-2	4149.241	0	4158.174	1	4064.151	-1	4045.858	-2	4054.888	-1	38.5
39.5	4167.380	2	4148.819	0	4157.983	0	4064.221	-1	4045.463	0	4054.726	0	39.5
40.5	4167.411	-3	4148.395	1	4157.787	-1	4064.286	-3	4045.060	-2	4054.558	-1	40.5
41.5	4167.446	0	4147.963	0	4157.589	1	4064.350	-2	4044.656	-1	4054.386	-2	41.5
42.5	4167.472	-1	4147.527	0	4157.385	0	4064.409	-1	4044.246	-2	4054.211	-1	42.5
43.5	4167.496	1	4147.088	1	4157.175	-1	4064.463	-1	4043.833	-1	4054.032	0	43.5
44.5			4146.642	0	4156.961	0	4064.511	-3	4043.416	-2	4053.849	1	44.5
45.5			4146.192	0	4156.744	1	4064.556	-3	4042.994	-1	4053.659	-1	45.5
46.5			4145.738	0	4156.517	-2	4064.601	1	4042.569	-1	4053.468	-1	46.5
47.5			4145.278	-1	4156.291	0	4064.641	4	4042.138	-2	4053.271	-1	47.5
48.5			4144.813	-1	4156.057	-1	4064.670	0	4041.706	0	4053.072	1	48.5
49.5			4144.346	1	4155.819	-1			4041.269	1	4052.867	0	49.5
50.5			4143.871	-1	4155.577	0			4040.826	0	4052.658	0	50.5
51.5			4143.395	2	4155.333	4			4040.380	0	4052.446	1	51.5
52.5			4142.912	2	4155.076	1			4039.930	1	4052.229	1	52.5
53.5			4142.420	-1	4154.819	1			4039.476	1	4052.007	1	53.5
54.5			4141.927	-1	4154.555	0			4039.016	-1	4051.781	1	54.5
55.5			4141.429	0	4154.287	0			4038.554	1	4051.551	0	55.5
56.5			4140.928	1	4154.013	-1			4038.087	0	4051.318	1	56.5
57.5			4140.419	0	4153.737	0			4037.617	1	4051.080	2	57.5
58.5			4139.904	-1	4153.451	-2			4037.142	1	4050.837	1	58.5
59.5			4139.386	-1	4153.164	-1			4036.662	1	4050.591	2	59.5
60.5					4152.872	1			4036.180	2	4050.340	2	60.5
61.5					4152.570	-3			4035.692	1	4050.084	1	61.5
62.5					4152.269	0			4035.199	0	4049.826	1	62.5
63.5					4151.963	3			4034.704	0	4049.563	2	63.5
64.5									4034.207	2	4049.296	2	64.5
65.5							4064.576		4033.703	3	4049.026	4	65.5
66.5							4064.533	1	4033.194	1	4048.748	1	66.5
67.5							4064.487	2	4032.683	1	4048.469	2	67.5
68.5							4064.436	4	4032.167	1	4048.186	3	68.5
69.5							4064.376	0	4031.647	2	4047.898	3	69.5
70.5							4064.320	5	4031.121	-1	4047.604	1	70.5
71.5							4064.246	-4	4030.591	-3	4047.309	3	71.5
72.5							4064.179	-3	4030.064	2	4047.007	1	72.5
73.5							4064.102	-6	4029.529	3	4046.703	2	73.5
74.5							4064.039	8	4028.987	1	4046.394	1	74.5

TABLE 1—*Continued*

J	R	O-C	P	O-C	Q	O-C	R	O-C	P	O-C	Q	O-C	J
75.5							4063.949	-1	4028.442	0	4046.079	-2	75.5
76.5							4063.865	2	4027.900	6	4045.765	1	76.5
77.5							4063.778	4	4027.346	3	4045.441	-2	77.5
78.5							4063.682	2	4026.789	2	4045.118	0	78.5
79.5							4063.581	-1	4026.228	1	4044.789	-1	79.5
80.5							4063.481	1	4025.661	-2	4044.456	-1	80.5
81.5							4063.369	-5	4025.093	-3	4044.118	-2	81.5
82.5							4063.260	-3	4024.523	-2	4043.776	-3	82.5
83.5							4063.152	4	4023.948	-1	4043.434	-1	83.5
84.5							4063.021	-9	4023.368	-3	4043.082	-3	84.5
85.5							4062.905	-3	4022.787	-2	4042.729	-4	85.5
86.5							4062.781	-1	4022.198	-4	4042.375	-2	86.5
87.5							4062.650	-1	4021.608	-3	4042.016	0	87.5
88.5							4062.515	-2	4021.013	-4	4041.651	-1	88.5
89.5							4062.377	-1	4020.419	-1			89.5
90.5							4062.234	-2	4019.816	-3			90.5
91.5							4062.089	-1	4019.211	-2			91.5
92.5							4061.941	1	4018.606	2			92.5
93.5							4061.786	0	4017.993	1			93.5
94.5							4061.630	1	4017.383	6			94.5
95.5							4061.470	3	4016.767	10			95.5
96.5							4061.313	11					96.5
97.5							4061.147	14					97.5
			$^4\Delta_{5/2}$ - $^4\Phi_{7/2}$ **1-1**						$^4\Delta_{5/2}$ - $^4\Phi_{7/2}$ **2-2**				
4.5			4034.303	1			4014.072	1			4012.793	2	4.5
5.5			4034.048	2			4014.272	-9	4011.495	6	4012.767	-1	5.5
6.5			4033.796	11			4014.480	-6	4011.231	3	4012.743	2	6.5
7.5			4033.515	-5			4014.672	-14	4010.968	4	4012.710	1	7.5
8.5			4033.248	-2	4035.244	7	4014.878	-5	4010.696	1	4012.673	-1	8.5
9.5			4032.974	-3	4035.199	1	4015.071	-4	4010.424	1	4012.629	-4	9.5
10.5			4032.708	8	4035.150	-4	4015.252	-12	4010.146	0	4012.580	-8	10.5
11.5					4035.108	2	4015.437	-11	4009.867	2	4012.538	-2	11.5
12.5			4032.134	2	4035.047	-7	4015.625	-3	4009.577	-3	4012.490	2	12.5
13.5	4038.386	-1	4031.841	-1	4034.998	0	4015.800	-4			4012.429	-1	13.5
14.5	4038.554	-6	4031.557	9	4034.934	-3	4015.979	4	4009.004	8	4012.368	-1	14.5
15.5	4038.720	-10	4031.252	3	4034.871	-1	4016.145	3	4008.705	7	4012.311	7	15.5
16.5	4038.888	-6	4030.953	5	4034.803	-1	4016.306	1	4008.395	-1	4012.236	1	16.5
17.5	4039.044	-11	4030.638	-2	4034.733	2	4016.466	2	4008.094	4	4012.159	-2	17.5
18.5	4039.202	-9	4030.329	-1	4034.653	-1	4016.618	0	4007.777	-2	4012.083	0	18.5
19.5	4039.365	2	4030.016	0	4034.573	0	4016.767	-2	4007.466	1	4011.998	-2	19.5
20.5	4039.508	-4	4029.695	-1	4034.486	-1	4016.911	-3	4007.145	-1	4011.914	0	20.5
21.5	4039.656	1	4029.376	3	4034.400	3			4006.824	1	4011.825	2	21.5
22.5	4039.798	2	4029.045	-1	4034.303	-1	4017.194	0	4006.497	1	4011.728	-1	22.5
23.5	4039.930	-1	4028.716	1	4034.207	1	4017.320	-7	4006.163	-1	4011.631	1	23.5
24.5			4028.378	-1	4034.106	2	4017.464	8	4005.828	0	4011.527	1	24.5
25.5	4040.191	2	4028.040	0	4033.998	0	4017.579	-2	4005.489	1	4011.419	0	25.5
26.5	4040.311	-1	4027.698	2	4033.886	-2	4017.702	1	4005.142	-3	4011.308	1	26.5
27.5	4040.431	0	4027.346	-3	4033.770	-3	4017.823	6	4004.795	-1	4011.189	-1	27.5
28.5			4026.997	1	4033.656	2	4017.931	2	4004.442	0	4011.073	3	28.5
29.5	4040.656	1	4026.642	2	4033.532	0	4018.037	2	4004.083	-3	4010.945	0	29.5
30.5	4040.762	0	4026.282	2	4033.405	1	4018.138	0	4003.725	1	4010.815	0	30.5
31.5			4025.917	1	4033.274	1	4018.239	3	4003.356	-2	4010.678	-4	31.5
32.5	4040.965	3	4025.547	-1	4033.140	2	4018.329	-1	4002.989	1	4010.544	1	32.5
33.5	4041.057	1	4025.178	3	4033.001	2	4018.419	0	4002.614	1	4010.400	0	33.5
34.5	4041.146	1	4024.799	1	4032.856	1	4018.507	3	4002.234	1	4010.254	1	34.5
35.5	4041.235	5	4024.419	1	4032.708	0	4018.574	-10	4001.849	0	4010.100	-1	35.5
36.5	4041.312	1	4024.034	1	4032.556	0	4018.655	-4	4001.462	1	4009.943	-1	36.5
37.5	4041.387	-1	4023.647	2	4032.399	-1	4018.737	8	4001.065	-2	4009.781	-2	37.5
38.5	4041.462	2	4023.253	1	4032.241	2	4018.793	-2	4000.667	-2	4009.617	1	38.5
39.5	4041.530	1	4022.852	-2	4032.075	0	4018.851	-4	4000.265	-1	4009.445	0	39.5
40.5	4041.597	3	4022.452	-1	4031.908	1	4018.911	1	3999.857	-1	4009.268	0	40.5
41.5	4041.651	-3	4022.047	0	4031.735	1	4018.962	1	3999.448	3	4009.088	1	41.5
42.5	4041.706	-3	4021.637	-1	4031.557	-1	4019.008	2	3999.030	3	4008.901	1	42.5
43.5	4041.761	0	4021.224	0	4031.376	-1	4019.048	3	3998.602	-1	4008.705	-3	43.5
44.5	4041.809	1	4020.807	0	4031.191	0			3998.174	0	4008.515	4	44.5
45.5	4041.847	-4	4020.385	0	4031.001	-1			3997.740	1	4008.308	0	45.5
46.5	4041.893	3	4019.959	0	4030.807	-1			3997.297	-3	4008.094	-6	46.5
47.5	4041.925	1	4019.529	-1	4030.613	2			3996.858	4	4007.882	-3	47.5
48.5	4041.956	1	4019.095	0	4030.408	-1					4007.660	-4	48.5
49.5	4041.980	-1	4018.655	-2	4030.202	-1					4007.437	-1	49.5
50.5			4018.214	-1	4029.991	-2					4007.203	-2	50.5

TABLE 1—*Continued*

J	R	O-C	P	O-C	Q	O-C	R	O-C	P	O-C	Q	O-C	J
51.5			4017.766	-2	4029.776	-2					4006.968	3	51.5
52.5			4017.317	-1	4029.556	-3							52.5
53.5			4016.861	-1	4029.334	-2							53.5
54.5			4016.401	-2	4029.111	2							54.5
55.5			4015.938	-2	4028.877	0							55.5
56.5			4015.471	-1	4028.640	-2							56.5
57.5			4015.000	-1	4028.402	1							57.5
58.5			4014.524	-1	4028.157	0							58.5
59.5			4014.043	-1	4027.900	-8							59.5
60.5			4013.559	-1	4027.655	0							60.5
61.5			4013.070	-2	4027.398	0							61.5
62.5			4012.580	2	4027.138	2							62.5
63.5			4012.083	2	4026.873	3							63.5
64.5			4011.581	1	4026.602	3							64.5
65.5			4011.073	-1	4026.328	3							65.5
66.5			4010.568	5	4026.047	2							66.5
67.5			4010.050	2	4025.765	4							67.5
68.5			4009.531	2	4025.476	3							68.5
69.5			4009.004	-1	4025.178	-2							69.5
70.5					4024.883	0							70.5
71.5					4024.579	-1							71.5
72.5					4024.270	-4							72.5
73.5					4023.948	-14							73.5
			$^4\Delta_{7/2}$ - $^4\Phi_{9/2}$ **0-0**						$^4\Delta_{7/2}$ -$^4\Phi_{9/2}$ **1-1**				
8.5			3888.262	-1	3890.257	-6							8.5
9.5	3892.694	0	3887.995	5	3890.223	-1			3864.734	4	3866.958	4	9.5
10.5	3892.880	-6	3887.710	-3	3890.178	-4			3864.458	2	3866.914	0	10.5
11.5	3893.077	1	3887.433	2	3890.133	-3			3864.180	2	3866.871	2	11.5
12.5	3893.261	1	3887.153	7	3890.083	-3			3863.898	2	3866.824	2	12.5
13.5	3893.439	-3	3886.852	-5	3890.027	-5			3863.620	10	3866.772	2	13.5
14.5	3893.619	0	3886.562	-2	3889.971	-3			3863.319	-1	3866.716	1	14.5
15.5	3893.793	1	3886.265	-3	3889.909	-3	3870.517	1	3863.028	1	3866.653	-2	15.5
16.5	3893.961	0	3885.966	0	3889.843	-4	3870.686	-1	3862.731	2	3866.588	-3	16.5
17.5	3894.130	4			3889.776	-1	3870.852	-1	3862.423	-4	3866.521	-3	17.5
18.5	3894.289	1	3885.352	-1	3889.703	0	3871.012	-4	3862.122	-1	3866.448	-4	18.5
19.5	3894.445	0	3885.042	1	3889.625	0	3871.181	7			3866.377	0	19.5
20.5	3894.600	1	3884.725	0	3889.546	2	3871.330	1	3861.496	-4	3866.294	-4	20.5
21.5	3894.749	1	3884.405	0	3889.461	3	3871.481	3	3861.178	-4	3866.211	-3	21.5
22.5	3894.895	1	3884.082	2	3889.371	2	3871.622	-3	3860.860	-2	3866.121	-5	22.5
23.5	3895.037	1	3883.751	-1	3889.277	1	3871.769	1	3860.533	-4	3866.032	-3	23.5
24.5	3895.176	3	3883.422	1	3889.181	2	3871.909	2	3860.208	0	3865.940	-1	24.5
25.5	3895.310	3			3889.081	2	3872.046	4	3859.873	-3	3865.842	0	25.5
26.5	3895.438	1	3882.747	2	3888.975	2	3872.172	-1	3859.540	0	3865.736	-4	26.5
27.5	3895.565	3	3882.404	3	3888.865	1	3872.298	-3	3859.198	-2	3865.631	-3	27.5
28.5	3895.687	2	3882.056	2	3888.754	2	3872.426	1	3858.855	-1	3865.520	-4	28.5
29.5	3895.805	3	3881.706	3	3888.638	3	3872.550	5	3858.510	0	3865.412	1	29.5
30.5	3895.919	2	3881.350	3	3888.516	1	3872.666	5	3858.161	1	3865.296	2	30.5
31.5	3896.029	3	3880.991	2	3888.391	1	3872.780	5	3857.808	2	3865.181	7	31.5
32.5	3896.133	0	3880.628	2	3888.262	0	3872.884	-1	3857.452	2			32.5
33.5	3896.238	2	3880.263	4	3888.131	1	3872.992	0	3857.093	3	3864.927	2	33.5
34.5	3896.335	2	3879.889	1	3887.995	1			3856.732	5	3864.798	3	34.5
35.5	3896.429	1	3879.513	-1	3887.855	1			3856.365	4	3864.666	4	35.5
36.5	3896.518	-1	3879.138	2	3887.710	0			3855.994	2	3864.529	2	36.5
37.5	3896.604	0	3878.755	1	3887.563	1			3855.624	3	3864.392	3	37.5
38.5	3896.686	-1	3878.367	0	3887.410	0			3855.249	1	3864.250	1	38.5
39.5	3896.764	-1	3877.977	-1	3887.255	0			3854.872	0	3864.111	4	39.5
40.5	3896.839	0	3877.582	-2	3887.093	-1					3863.960	-2	40.5
41.5	3896.910	0	3877.185	-1	3886.928	-3					3863.813	-1	41.5
42.5	3896.973	-3	3876.783	-2	3886.761	-2			3853.730	-2	3863.662	-3	42.5
43.5	3897.039	0	3876.376	-3	3886.589	-3			3853.345	-4		0	43.5
44.5	3897.094	-4	3875.969	0	3886.413	-3			3852.959	-4	3863.357	-6	44.5
45.5	3897.151	0	3875.553	-3	3886.235	-2			3852.575	-1	3863.202	-6	45.5
46.5	3897.199	-3	3875.135	-4	3886.050	-3					3863.050	-3	46.5
47.5	3897.245	-3	3874.715	-3	3885.863	-3			3851.792	-6	3862.894	-2	47.5
48.5	3897.285	-4	3874.289	-3					3851.404	-3	3862.731	-7	48.5
49.5	3897.330	2	3873.861	-2	3885.475	-4			3851.016	1	3862.578	1	49.5
50.5	3897.364	3	3873.427	-3	3885.277	-3			3850.624	3	3862.423	6	50.5
51.5	3897.390	-2	3872.992	-1	3885.072	-4			3850.233	6	3862.262	7	51.5
52.5	3897.415	-3	3872.550	-2	3884.867	-2			3848.808*	-1022	3861.066*	-1024	52.5
53.5	3897.439	0	3872.105	-2	3884.655	-2			3848.398*	-1035	3860.887*	-1038	53.5
54.5			3871.658	-1	3884.440	-2			3847.985*	-1049	3860.708*	-1050	54.5

TABLE 1—*Continued*

J	R	O-C	P	O-C	Q	O-C	R	O-C	P	O-C	Q	O-C	J
55.5			3871.206	-1	3884.222	-1			3847.566*	-1066			55.5
56.5			3870.750	0	3884.000	1			3847.142*	-1086	3860.332*	-1085	56.5
57.5			3870.291	0	3883.775	2			3846.721*	-1100	3860.139*	-1104	57.5
58.5			3869.828	0	3883.544	1			3846.292*	-1120	3859.943*	-1122	58.5
59.5			3869.363	2	3883.312	3			3845.862*	-1136	3859.747*	-1137	59.5
60.5			3868.894	3	3883.077	6			3845.428*	-1153	3859.540*	-1158	60.5
61.5			3868.420	3	3882.834	4			3845.001*	-1157	3859.348*	-1159	61.5
62.5			3867.944	4	3882.590	4			3844.564*	-1165	3859.144*	-1166	62.5
63.5			3867.464	4	3882.342	3			3844.126*	-1167	3858.942*	-1162	63.5
64.5			3866.982	5	3882.095	7					3858.740*	-1151	64.5
65.5			3866.496	5	3881.839	4					3858.536*	-1132	65.5
66.5			3866.005	3	3881.580	2					3858.333*	-1101	66.5
67.5			3865.520	8	3881.325	4					3858.129*	-1057	67.5
68.5			3865.020	1	3881.062	2					3857.927*	-997	68.5
69.5			3864.529	4	3880.800	3					3857.718*	-926	69.5
70.5			3864.028	-1	3880.531	-2					3857.516*	-827	70.5
71.5			3863.532	0	3880.263	-4					3857.306*	-716	71.5
72.5			3863.028	-5	3879.998	-3					3857.093*	-581	72.5
73.5			3862.529	-6	3879.729	-5					3856.869*	-429	73.5
74.5			3862.031	-5	3879.461	-5					3856.665*	-224	74.5
75.5			3861.528	-9	3879.191	-9					3856.462*	18	75.5
76.5			3861.031	-9	3878.929	-5					3856.260*	301	76.5
77.5			3860.533	-12	3878.664	-6					3856.038*	609	77.5
78.5					3878.400	-8					3855.830*	981	78.5
79.5					3878.148	0					3855.624*	1411	79.5
80.5					3877.898	6					3855.425*	1909	80.5
81.5					3877.647	7							81.5
82.5					3877.404	10							82.5

$^4\Delta_{7/2}$ -$^4\Phi_{9/2}$ **2-2**

J	R	O-C	P	O-C	Q	O-C	J	R	O-C	P	O-C	Q	O-C
19.5					3842.981	13	56.5			3823.822	1	3836.949	1
20.5					3842.888	9	57.5			3823.351	2	3836.710	3
21.5	3848.032	5			3842.796	10	58.5			3822.875	1	3836.466	4
22.5	3848.168	5	3837.448	-1	3842.694	4	59.5			3822.398	5	3836.219	6
23.5	3848.298	4	3837.120	4	3842.594	6	60.5			3821.913	3	3835.964	4
24.5	3848.424	2	3836.780	2	3842.485	2	61.5			3821.426	5	3835.709	7
25.5	3848.548	3	3836.440	4	3842.371	-3	62.5			3820.937	8	3835.449	8
26.5	3848.662	-2	3836.087	-2	3842.259	-1	63.5			3820.442	9	3835.193*	19
27.5	3848.779	0	3835.735	-4	3842.142	-1	64.5			3819.951*	19		
28.5	3848.888	-1	3835.382	-3	3842.015	-5	65.5					3834.606*	-23
29.5	3848.994	-2			3841.892	-2	66.5					3834.334*	-17
30.5	3849.098	0	3834.660	-3	3841.762	-2	67.5					3834.059	-8
31.5			3834.293	-4	3841.627	-3	68.5					3833.772	-7
32.5			3833.923	-3	3841.487	-5	69.5					3833.480	-7
33.5	3849.378	-2	3833.547	-4	3841.348	-1	70.5					3833.184	-7
34.5	3849.460	-5			3841.201	-1	71.5					3832.884	-6
35.5	3849.542	-5	3832.790	1			72.5					3832.578	-7
36.5	3849.618	-6	3832.399	-3	3840.896	-2	73.5					3832.270	-5
37.5	3849.698	0	3832.008	-4	3840.736	-3	74.5			3814.687	-2	3831.957	-4
38.5	3849.767	1	3831.620	3	3840.572	-4	75.5			3814.140	-2		
39.5	3849.832	0	3831.216	-2	3840.408	-1	76.5			3813.591	2	3831.317	-2
40.5	3849.895	2	3830.814	-1	3840.238	0	77.5					3830.989	-3
41.5	3849.950	0	3830.409	1	3840.064	1	78.5			3812.470	-2	3830.661	1
42.5	3850.003	1	3829.997	1	3839.886	2	79.5			3811.904	-2	3830.323	0
43.5	3850.057	6	3829.584	2	3839.700	0	80.5			3811.339	2	3830.005	22
44.5	3850.100	4	3829.164	1	3839.514	1	81.5			3810.765	2	3829.640	2
45.5			3828.739	0	3839.323	1	82.5					3829.291	2
46.5			3828.312	-1	3839.129	3	83.5			3809.596	-6	3828.940	5
47.5			3827.881	0	3838.926	-1	84.5			3809.022	5	3828.580	3
48.5			3827.448	2	3838.726	3	85.5			3808.427	1	3828.224	8
49.5			3827.008	0	3838.518	2	86.5			3807.834	2	3827.854	5
50.5			3826.563	-1	3838.308	4	87.5					3827.476	-3
51.5			3826.117	-1			88.5			3806.634	2	3827.108	2
52.5			3825.665	-1			89.5			3806.026	1		
53.5			3825.211	0	3837.646	2	90.5			3805.413	-3		
54.5			3824.758	7	3837.419	2	91.5			3804.794	-9		
55.5			3824.290	2	3837.187	3							

TABLE 2

Rotational Constants (in cm^{-1}) for the $C^4\Delta - X\,^4\Phi$ Bands of ZrCl

Transition		T_{vv}	B_v'	$10^8 \times D_v'$	$10^2 \times p_v'$	$10^7 \times p_{Dv}'$	B_v''	$10^8 \times D_v''$	$10^{11} \times H_v''$	$10^{15} \times L_v''$
$^4\Delta_{1/2}$-$^4\Phi_{3/2}$	0-0	4300.38412(50)	0.1171518(47)	5.376(39)	-1.2089(15)	2.671(26)	0.1201246(48)	15.890(63)	0.9732(88)	-0.3613(51)
	1-1	4280.20175(44)	0.1166470(56)	5.502(54)	-0.8018(16)	0.886(26)	0.1193543(55)	8.327(54)	0.1311(16)	--
	2-2	4259.50793(88)	0.1161193(93)	5.73(23)	-0.63227(93)	--	0.1187165(93)	6.99(24)	0.114(40)	-0.067(33)
$^4\Delta_{3/2}$-$^4\Phi_{5/2}$	0-0	4203.4231(15)	0.117249(19)	6.06(57)	--	--	0.120140(19)	9.90(60)	12.936(63)	--
	1-1	4186.44147(90)	0.1166852(84)	5.23(17)	--	--	0.1199711(91)	29.01(30)	3.381(65)	-2.015(64)
	2-2	4161.84049(43)	0.1161620(69)	5.37(18)	--	--	0.1185871(69)	6.58(18)	0.218(14)	--
$^4\Delta_{5/2}$-$^4\Phi_{7/2}$	0-0	4058.01515(37)	0.1174188(40)	5.354(31)	--	--	0.1194671(39)	4.792(32)	-0.04289(98)	--
	1-1	4035.40606(55)	0.1168957(74)	5.53(14)	--	--	0.1189822(74)	5.95(14)	0.0882(74)	--
	2-2	4012.84360(62)	0.116336(12)	4.80(40)	--	--	0.118448(12)	6.27(45)	1.387(59)	--
$^4\Delta_{7/2}$-$^4\Phi_{9/2}$	0-0	3890.42399(73)	0.1175978(77)	5.50(13)	--	--	0.1196049(81)	8.43(19)	1.013(31)	-1.206(24)
	1-1	3867.1431(12)	0.1170502(72)	5.19(16)	--	--	0.1189395(89)	-4.66(59)	-7.34(24)	9.57(33)
	2-2	3843.8346(19)	0.1165100(82)	5.349(92)	--	--	0.1186911(87)	8.52(17)	0.470(28)	-0.226(16)

Note: The numbers in parentheses are one standard deviation in the last two digits.

side of the 0–0 band of the $^4\Delta_{3/2}-^4\Phi_{5/2}$ subband and these lines also probably belong to another transition. The $^4\Delta_{3/2}-^4\Phi_{5/2}$ subband was difficult to assign because of a global perturbation of the $^4\Phi_{5/2}$ spin component and the extra lines. No extra heads have been observed in the regions of the $^4\Delta_{5/2}-^4\Phi_{7/2}$ and $^4\Delta_{7/2}-^4\Phi_{9/2}$ subbands. The 0–0, 1–1, and 2–2 bands of all the subbands were rotationally analyzed. A part of the structure of the 0–0 band of the $^4\Delta_{7/2}-^4\Phi_{9/2}$ subband is presented in Fig. 2.

As is often the case, no transitions having $\Delta\Sigma \neq 0$ were observed and the spin–orbit intervals could not be determined directly. The subbands of the different spin components were fitted separately using a simple effective term energy expression:

$$F_v(J) = T_v + B_vJ(J+1) - D_v[J(J+1)]^2 + H_v[J(J+1)]^3 + L_v[J(J+1)]^4 \pm 1/2[p_v(J+1/2) + p_{Dv}(J+1/2)^3]. \quad [1]$$

The rotational lines were weighted according to resolution, extent of blending, and the effect of perturbations. Perturbed lines were not included in the fit and the badly blended lines were heavily deweighted. Occasionally higher-order effective rotational constants H_v and L_v are required in some spin components to obtain a satisfactory fit. The higher-order rotational constants clearly have no mechanical meaning but they reflect interactions with the other spin components and other electronic states. The observed line positions for the different subbands are provided in Table 1 and the molecular constants for the different bands are provided in Table 2. The e/f parity assignment in the $^4\Delta_{1/2}-^4\Phi_{3/2}$ subband was made arbitrarily to provide a negative Ω-doubling constant p_v in the $^4\Delta_{1/2}$ state. The higher-order Ω-doubling constant p_{Dv} was also determined for the $v = 0$ and 1 vibrational levels of this state.

DISCUSSION

Although the bands of ZrCl in the visible and near-ultraviolet regions have been known for decades, the identity of the ground state is still an open question. The previously suggested $^4\Sigma^-$ ground state is not consistent with the recently observed $X^4\Phi$ ground state of TiF (*8*) and TiCl (*9*). We suspect that Jordan *et al.* (*2*) have, in fact, measured a $^4\Delta-X^4\Phi$ or a $^4\Gamma-X^4\Phi$ transition in the region 400–415 nm. The present $^4\Delta-^4\Phi$ transition of ZrCl is analogous to the $C^4\Delta-X^4\Phi$ transition of TiCl (*9*). Since no theoretical calculations are available for ZrCl, we have used the recent calculations for the isovalent TiF (*6*) molecule as a guide. As predicted by Harrison for TiF (*6*), there are quartet and doublet manifolds of electronic states, of which a $^4\Phi$ state is the lowest in energy. Among the doublet states, a $^2\Phi$ state is lowest at about 5200 cm^{-1} above the ground $X^4\Phi$ state. Although the $^2\Phi-X^4\Phi$ separation will be different for TiF and TiCl, the general pattern of energy levels should be similar. For ZrCl, the doublet–quartet separation may well change considerably and it is possible that a $^2\Phi$ or even a $^2\Delta$ state could become the ground state. Further experimental and theoretical work is necessary to confirm the ground state assignment for ZrCl.

Several perturbations have been observed in the spectrum of the ZrCl $C^4\Delta-X^4\Phi$ transition. The excited $C^4\Delta$ state is unperturbed. The ground $X^4\Phi_{3/2}$ spin component with $v = 1$ is affected by a local perturbation at about $J'' = 67.5$ and the $v = 0$ level is affected by a global perturbation which shifts $B_{\rm eff}$ to a higher value. The $v = 0$ and 1 vibrational levels of the $X^4\Phi_{5/2}$ spin component are affected by strong global perturbations. Local perturbations are also present in the $v = 1$ vibrational level of the $X^4\Phi_{9/2}$ spin component at $J'' = 52.5$ and probably in the $v = 2$ vibrational level at $J'' = 66.5$. Clearly there are one or more low-lying electronic states which interact with the $X^4\Phi_{3/2}$, $X^4\Phi_{5/2}$, and $X^4\Phi_{9/2}$ spin components.

In the absence of $\Delta v \neq 0$ bands, only limited vibrational data could be extracted from the present analysis. As seen in Table 2, the excited $^4\Delta_{1/2}$ spin component has large Ω-doubling, presumably because of interaction with another state such as a $^2\Pi$ state. This observation is in contrast to the results for TiCl where no Ω-doubling was observed in the $C^4\Delta$ state. The observation in ZrCl of the transition analogous to the $G^4\Phi-X^4\Phi$ transition of TiF (*8*) and TiCl (*9*) will provide more information about the electronic structure. So far this transition has not been detected.

The Hund's case (*a*) equilibrium constants were derived by averaging the effective rotational constants of each spin component. The relationship between the effective constants and Hund's case (*a*) constants for $^4\Delta$ states (*14*) and $^4\Phi$ states (*8*) is well known. For the $C^4\Delta$ state the $B_{\rm eff}$ values for each vibrational level were averaged and then $B'_e = 0.11769$ cm^{-1} and $\alpha'_e = 0.00054$ cm^{-1} were determined. An estimate for the spin–orbit constant $A'_0 = 62$ cm^{-1} was made from the different $B_{\rm eff}$ values. The $X^4\Phi$ state shows the effects of both global and local perturbations so the procedure described above was used only for the relatively unaffected $X^4\Phi_{9/2}$ and $X^4\Phi_{7/2}$ spin components. The values of $B''_e = 0.1196$ cm^{-1}, $\alpha''_e = 0.0004$ cm^{-1}, and $A''_0 = 69$ cm^{-1} were obtained for the $X^4\Phi$ state. The B'_e and B''_e values provide $r'_e = 2.3852$ Å and $r''_e = 2.3661$ Å for the excited and ground states, respectively.

The electron configurations of the observed states are expected to be the same as those for the isovalent TiCl molecule. Following the simple ionic bonding model, the $C^4\Delta$ and $X^4\Phi$ states of ZrCl arise from $\pi^2\delta^1$ and $\sigma^1\pi^1\delta^1$ configurations on the metal atom, respectively.

CONCLUSIONS

We have recorded the emission spectrum of ZrCl in the region 3000–10 000 cm^{-1} using a Fourier transform spectrometer. Four groups of prominent bands with the 0–0 *R* heads at 4305.7, 4208.0, 4064.7, and 3897.4 cm^{-1} have been assigned as the $^4\Delta_{1/2}-{}^4\Phi_{3/2}$, $^4\Delta_{3/2}-{}^4\Phi_{5/2}$, $^4\Delta_{5/2}-{}^4\Phi_{7/2}$, and $^4\Delta_{7/2}-{}^4\Phi_{9/2}$ subbands of the $C^4\Delta - X\,^4\Phi$ transition analogous to the same transition of TiCl in the region 3100–3400 cm^{-1} (*9*). Each of the 0–0 bands is followed by weaker 1–1, 2–2, and 3–3 vibrational bands to lower wavenumbers. A rotational analysis of several of these bands has been obtained and the molecular constants have been determined. The lowest $^4\Phi$ state most probably is the ground state of this molecule but we do not have any direct evidence to prove this. Further experimental and theoretical work will be necessary to prove our proposed assignment.

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