Infrared emission spectroscopy of a new $^2\Sigma$–$^2\Sigma$ system of TiCl

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Abstract

The spectra of TiCl have been reinvestigated in the 4200–8500 cm^{-1} region using the 1-m Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. The molecules were excited in a microwave discharge lamp operated with 3.0 Torr of He and a trace of TiCl$_4$ vapor, and the spectra were recorded at a resolution of 0.01 cm^{-1}. Three new bands with origins near 6938.9, 6900.2, and 6861.7 cm^{-1} have been assigned as the 0–0, 1–1, and 2–2 bands of a new $^2\Sigma$–$^2\Sigma$ transition. This assignment is supported by our recent ab initio calculations on TiCl and ZrCl [J. Chem. Phys. 114 (2001) 3977]. A rotational analysis of these bands has been carried out and spectroscopic constants have been extracted for the $^2\Sigma$ states.
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1. Introduction

Titanium-containing molecules are species of astrophysical importance [1]. Because of the relatively high abundance of titanium at the surface of cool stars, diatomic molecules such as TiO [2–6] and perhaps TiH [7–11] have been observed in the atmospheres of cool M-type and S-type stars, and sun spots. Titanium halides such as TiF and TiCl might also be expected to be present. So far no meaningful search has been made for these molecules partly because the spectroscopic data for the titanium halide molecules have been very limited. For example, the complex spectra of TiCl in the 400–420 nm region have been known since 1907 [12] and several attempts have been made on the vibrational and electronic assignments [13–20], providing contradictory results. The identity of even the ground state of TiCl remained in question for many years with some groups suggesting a $^4\Sigma^-$ ground [14,15] state, while others proposed a $^2\Delta$ ground state [18–20]. This uncertainty has been sorted out recently by the experimental investigation of TiCl in the near infrared [21,22], visible [23], and submillimeter wave regions [24].

The TiCl bands observed in the 3000–13500 cm^{-1} region using a Fourier transform spectrometer have been classified into three quartet–quartet transitions, $C^4\Delta$–$X^4\Phi$, $G^4\Phi$–$X^4\Phi$, and $G^4\Phi$–$C^4\Delta$ [21] and a doublet-doublet transition, [12.8]$^2\Phi$-$a^2\Phi$ [22], with the $X^4\Phi$ state being the ground state. The bands located in the 400–420 nm region were recently investigated at high resolution by Imajo et al. [23] using a Fourier transform spectrometer and were assigned to a $^4\Gamma$–$X^4\Phi$ transition [24]. The assignment of the ground state as a $^4\Phi$ state has been confirmed by the observation of pure rotational transitions in the four spin components using submillimeter wave spectroscopy by Maeda et al. [24]. Several theoretical studies of TiCl have also been reported in recent years [25–29], confirming a $^4\Phi$ ground state.

In our previous studies of TiCl [21,22], we noted the presence of several additional weak and complex bands in the 4000–12000 cm^{-1} region, but they were left unassigned. To advance the analysis of unassigned bands in the 4000–8500 cm^{-1} interval this region was re-recorded at an improved resolution of 0.01 cm^{-1}. A group of new bands located in the 6700–7000 cm^{-1} region has

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been identified as a $^2\Sigma$–$^2\Sigma$ transition of TiCl. A rotational analysis of the 0–0, 1–1, and 2–2 bands of the new transition has been obtained, and forms the subject of the present paper. This assignment will be discussed in the light of our ab initio calculations for TiCl and ZrCl [29].

2. Experimental details

The details of the experimental set up used have been provided in our previous publications [21,22]. The molecules were produced in a microwave discharge lamp using a mixture of $TiCl_4$ vapor and about 3.0 Torr of He. The discharge tube was made of quartz and had an outside diameter of 12 mm. The emission from the lamp was sent directly into the entrance aperture of the 1-m Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory at Kitt Peak. The spectra in the 4200–8500 cm^{-1} region were recorded using a CaF_2 beam splitter, liquid nitrogen-cooled InSb detectors, and green glass filters. A total of five scans co-added in about 35 min of integration at a resolution of 0.01 cm^{-1} was sufficient to obtain a spectrum with a signal-to-noise ratio suitable for rotational analysis.

The line positions were extracted from the observed spectra using a data reduction program called PC-DE-COMP developed by Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature. The branches in the different bands were sorted using a color Loomis–Wood program running on a PC computer. Since this new spectrum lacked strong atomic or molecular lines needed for calibration, the spectrum was calibrated by transferring the calibration from a previously recorded spectrum [21] using common atomic and molecular lines. The previous spectrum was calibrated using the measurements of the 1–0 vibration–rotation band of HCl [30]. The TiCl lines

in the 0–0 band of the $^2\Sigma$–$^2\Sigma$ transition appear with a maximum signal-to-noise ratio of about eight and have a typical line width of about 0.035 cm^{-1}. The absolute accuracy of the wavenumber scale is expected to be of the order of ± 0.003 cm^{-1}, however, the accuracy of the measurements for the weaker and overlapped lines is limited to ± 0.005 cm^{-1}.

3. Results and discussion

The TiCl bands assigned to the new transition are located in the 6700–7000 cm^{-1} interval and consist of 0–0, 1–1, and 2–2 bands with their origins located near 6938.9, 6900.2, and 6861.7 cm^{-1}, respectively. No off-diagonal vibrational bands were identified. The lines belonging to both major isotopomers $^{48}Ti^{35}Cl$ and $^{48}Ti^{37}Cl$ have been identified and a rotational analysis of the 0–0, 1–1, and 2–2 bands of $^{48}Ti^{35}Cl$ and the 0–0 band of $^{48}Ti^{37}Cl$ has been obtained. The spectrum of each band consists of two R- and two P-branches as expected for a $^2\Sigma$–$^2\Sigma$ transition. A part of the 0–0 and 1–1 bands near the R heads is illustrated in Fig. 1.

The rotational assignment in different bands was straight forward by comparing the combination differences for the e- and f-parity levels of the lower and upper states. The e/f parities were assigned arbitrarily. In this manner, we found two sets of lower state combination differences with very similar magnitudes and with a small difference due to the small spin splitting in the lower state. The rotational constants for the individual vibrational levels were determined by fitting the observed line positions to the energy level expression for a $^2\Sigma$ state utilizing the effective Hamiltonian of Brown et al. [31]. The matrix elements for a $^2\Sigma$ Hamiltonian are listed by Douay et al. [32]. The constants T_v, B_v, D_v, H_v, γ_v, γ_{Dv}, and γ_{Hv} were determined for the excited state, while only B_v, D_v, and γ_v were required in the lower $^2\Sigma$ state. For the $v' = 0$ vibrational level of $^{48}Ti^{37}Cl$ the
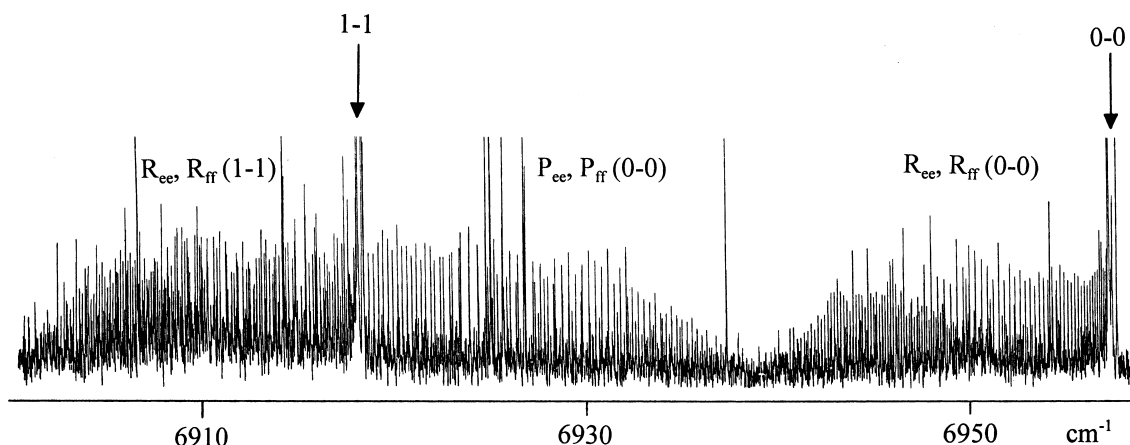

Fig. 1. A portion of the new system of TiCl near the R heads of the 0–0 and 1–1 bands.

Table 1
Observed line positions (in cm^{-1}) for the new $^2\Sigma$–$^2\Sigma$ system of TiCl

N	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c
	^{48}Ti^{35}Cl (0–0)								^{48}Ti^{35}Cl (1–1)							
1	6939.728	1														
2	6940.153	−1							6901.470	5						
3	6940.572	−6			6939.585	−2			6901.893	1						
4	6940.997	−3			6939.785	−3			6902.322	8						
5	6941.417	−2			6939.988	1			6902.733	−0			6901.247	9	6897.938	−3
6					6940.183	−1			6903.150	1			6901.424	−2	6897.489	2
7	6942.250	5	6937.204	11	6940.379	1	6935.750	−2	6903.563	3	6898.533	2	6901.612	2		
8	6942.658	5	6936.967	10	6940.572	3	6935.298	1	6903.969	2	6898.300	1	6901.794	1	6896.571	−0
9	6943.052	−5	6936.723	4	6940.761	1	6934.843	2	6904.373	1	6898.065	1	6901.974	1	6896.108	−1
10	6943.464	6	6936.480	4	6940.948	0	6934.395	12	6904.771	−0	6897.823	−2	6902.152	3	6895.645	1
11	6943.859	4	6936.232	2	6941.132	−1	6933.921	−1	6905.168	1	6897.586	4	6902.322	−2	6895.179	2
12	6944.249	1	6935.982	3	6941.314	−2	6933.458	−1	6905.559	0	6897.337	2	6902.499	2	6894.712	4
13	6944.639	2	6935.728	2	6941.497	−1	6932.995	0	6905.949	3	6897.083	−1	6902.668	1	6894.236	−1
14	6945.025	3	6935.469	0	6941.675	−2	6932.528	1	6906.330	1	6896.832	3	6902.835	0	6893.761	−1
15	6945.409	5	6935.212	4	6941.856	1	6932.059	1	6906.706	−0	6896.571	1	6903.002	1	6893.284	−2
16	6945.784	3	6934.945	2	6942.029	−2	6931.586	−2	6907.083	2	6896.308	1	6903.166	1	6892.807	−1
17	6946.155	2	6934.678	4	6942.203	−3	6931.106	−10	6907.447	−3	6896.042	4	6903.325	−1	6892.325	−2
18	6946.523	1	6934.395	−6	6942.376	−2	6930.641	−1	6907.817	2			6903.487	1	6891.844	−1
19	6946.886	1	6934.127	4	6942.549	0	6930.163	−3	6908.174	−0	6895.492	3	6903.643	−0	6891.358	−2
20	6947.244	−0	6933.844	2	6942.717	−2	6929.690	0	6908.525	−4	6895.207	−1	6903.796	−3	6890.872	−2
21	6947.603	4	6933.559	3	6942.884	−2	6929.207	−4	6908.882	3	6894.923	1	6903.950	−2		
22	6947.952	3	6933.269	3	6943.052	−1	6928.729	−2	6909.221	−3	6894.630	−1	6904.104	−1	6889.894	−1
23	6948.296	1	6932.972	0	6943.213	−4	6928.246	−3	6909.560	−3	6894.335	−1	6904.254	−1	6889.402	−2
24	6948.635	1	6932.674	2	6943.378	−3	6927.764	−2	6909.895	−2	6894.036	1	6904.400	−2		
25	6948.968	−1	6932.369	1	6943.539	−3	6927.277	−4	6910.227	0	6893.729	−0	6904.548	−2	6888.413	−2
26	6949.302	2	6932.059	0	6943.701	−2	6926.794	−2	6910.548	−3	6893.419	1	6904.694	0	6887.917	−1
27	6949.625	1	6931.747	2	6943.859	−3	6926.305	−4	6910.865	−3	6893.102	−1	6904.835	−2	6887.419	−1
28	6949.944	1	6931.428	2	6944.018	−2	6925.818	−2	6911.178	−2	6892.781	0	6904.978	−1	6886.918	−1
29	6950.257	−2	6931.106	3	6944.175	−2	6925.330	−2	6911.485	−2	6892.453	−2	6905.118	−1	6886.422	3
30	6950.567	0	6930.774	−0	6944.330	−2	6924.838	−3	6911.786	−2	6892.122	−0	6905.257	0	6885.915	0
31	6950.869	−1	6930.441	0	6944.484	−2	6924.346	−4	6912.081	−1	6891.785	0	6905.395	1	6885.409	−2
32	6951.167	−1	6930.101	0	6944.639	0	6923.854	−2	6912.369	−2	6891.441	−0	6905.528	−1	6884.906	1
33	6951.458	−1	6929.756	−0	6944.789	−1	6923.359	−4	6912.653	−1	6891.091	−1	6905.662	−1	6884.395	−3
34	6951.743	−2	6929.406	−1	6944.940	−1	6922.867	−1	6912.932	1	6890.737	0	6905.792	−2	6883.888	−1
35	6952.024	−1	6929.051	−0	6945.090	0	6922.371	−1	6913.202	0	6890.368	−9	6905.924	−2	6883.379	−1
36	6952.297	−2	6928.688	−2	6945.236	−2	6921.874	−1	6913.466	0	6890.009	−1	6906.054	−0	6882.868	−0
37	6952.565	−2	6928.322	−0	6945.384	−1	6921.377	−1	6913.722	−0	6889.639	2	6906.182	−0	6882.355	−1
38	6952.828	−1	6927.949	−1	6945.530	−1	6920.878	−1	6913.972	−1	6889.258	−0	6906.307	−2	6881.840	−2
39	6953.082	−2	6927.571	0	6945.676	0	6920.379	−1	6914.217	−0	6888.874	1	6906.431	−2	6881.328	1
40	6953.331	−2	6927.184	−2	6945.821	2	6919.880	1	6914.455	0	6888.481	−0			6880.811	1
41	6953.573	−2	6926.794	−2	6945.962	1	6919.379	1	6914.687	1	6888.085	2	6906.677	−1	6880.296	2
42	6953.808	−2	6926.397	−2	6946.102	−1	6918.876	1	6914.908	−2	6887.678	−1	6906.799	0	6879.776	1
43	6954.037	−3	6925.995	−0	6946.243	1	6918.374	1	6915.125	−1	6887.267	0	6906.917	−1	6879.256	1
44	6954.261	−1	6925.582	−4	6946.383	1	6917.869	1	6915.336	1	6886.848	−1	6907.036	0	6878.735	1
45	6954.475	−3	6925.168	−2	6946.523	3	6917.367	4	6915.538	0	6886.422	−3	6907.152	0	6878.212	−0
46	6954.685	−1			6946.658	2	6916.859	2	6915.732	0	6885.994	1	6907.267	1	6877.693	4
47	6954.885	−2	6924.317	−2	6946.796	4	6916.352	2	6915.928	8	6885.554	−1	6907.379	−0	6877.167	3
48	6955.080	−2	6923.881	−2	6946.927	2	6915.846	3	6916.099	−1	6885.109	−1	6907.493	2	6876.640	2
49	6955.269	−0	6923.438	−2	6947.064	5	6915.336	2	6916.269	−3	6884.656	−1	6907.601	−0	6876.114	1
50	6955.447	−1	6922.990	−0	6947.195	4	6914.828	3	6916.438	2	6884.198	1	6907.710	0	6875.583	−0
51	6955.619	−2	6922.533	−1	6947.325	4	6914.318	3	6916.592	−1	6883.731	1	6907.817	−1	6875.052	−2
52	6955.784	−1	6922.068	−3	6947.454	4	6913.808	4	6916.748	5	6883.254	−1	6907.925	2	6874.524	1
53	6955.942	−0	6921.599	−1	6947.583	5	6913.295	4	6916.884	0	6882.775	1	6908.028	1	6873.995	4
54	6956.091	−1	6921.122	−1	6947.708	3	6912.783	5	6917.012	−4	6882.284	0	6908.132	3	6873.453	−5
55	6956.235	1	6920.636	−2	6947.833	3	6912.266	2	6917.144	3	6881.784	−3	6908.228	−1	6872.925	1
56	6956.369	1	6920.145	−1	6947.952	−2	6911.750	2	6917.255	−3	6881.281	−0	6908.328	−0	6872.387	−1
57	6956.493	−0	6919.646	−0	6948.079	3	6911.234	2	6917.367	1	6880.767	−2	6908.426	1	6871.853	2
58	6956.611	−0	6919.139	−0	6948.199	3	6910.717	3	6917.468	1	6880.251	3	6908.525	4	6871.317	4
59	6956.720	−1	6918.624	0	6948.319	4	6910.200	4	6917.569	11	6879.714	−5	6908.612	−1	6870.776	3
60	6956.821	−2	6918.099	−2	6948.434	1	6909.682	5	6917.645	5	6879.184	1	6908.709	4	6870.235	3
61	6956.919	2	6917.569	−2	6948.550	1	6909.157	1	6917.716	2	6878.640	2	6908.796	2	6869.695	6
62	6957.004	3	6917.031	−2	6948.663	1	6908.635	2	6917.780	0	6878.080	−5	6908.882	1	6869.145	1

Table 1 (*continued*)

N	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c
63	6957.083	5	6916.486	−1	6948.774	−1	6908.112	2	6917.841	4	6877.526	3			6868.602	4
64			6915.928	−5	6948.884	−1	6907.583	−1	6917.893	9	6876.956	2			6868.056	6
65			6915.370	−0	6948.993	0	6907.059	1	6917.925	3	6876.374	−2			6867.512	11
66	6957.257	1	6914.802	2	6949.101	1			6917.960	8	6875.790	1			6866.937	−13
67	6957.301	3	6914.217	−5	6949.201	−3	6905.999	−2	6917.980	8	6875.193	−1			6866.388	−9
68	6957.338	8	6913.637	2	6949.302	−4	6905.465	−4	6917.987	3	6874.590	1			6865.835	−7
69	6957.363	9	6913.042	2	6949.400	−5	6904.935	−2	6917.987	2	6873.970	−7			6865.280	−6
70	6957.372	2	6912.439	3	6949.500	−3	6904.400	−2	6917.980	3	6873.357	1			6864.722	−4
71	6957.372	−4	6911.825	1	6949.594	−4	6903.867	1	6917.960	−0	6872.727	2			6864.163	−3
72	6957.372	−0	6911.205	1	6949.688	−3	6903.325	−2	6917.925	−8	6872.086	1			6863.596	−6
73	6957.363	3	6910.577	2	6949.774	−6	6902.785	−3	6917.893	−4	6871.438	2			6863.035	−1
74	6957.338	0	6909.939	3	6949.863	−4	6902.242	−3	6917.841	−10	6870.776	−3			6862.460	−9
75	6957.301	−6	6909.288	−1	6949.944	−7	6901.697	−3	6917.783	−12	6870.109	−3			6861.893	−6
76	6957.257	−10	6908.635	2	6950.026	−6	6901.149	−5	6917.719	−10	6869.437	2			6861.322	−4
77			6907.970	1			6900.599	−5	6917.645	−8	6868.748	−2			6860.746	−4
78			6907.297	2	6950.182	−4	6900.050	−2	6917.569	1	6868.056	2			6860.172	0
79	6957.083	−4	6906.616	3	6950.257	−1	6899.493	−4	6917.468	−4	6867.348	−2			6859.591	0
80	6957.004	−4	6905.924	3	6950.324	−2	6898.938	−2	6917.367	2	6866.633	−3			6859.008	1
81	6956.919	−1	6905.217	−2	6950.393	2	6898.376	−4	6917.255	7	6865.919	6			6858.422	2
82	6956.821	0	6904.510	0	6950.456	4	6897.823	5	6917.119	−3	6865.181	3			6857.840	10
83	6956.720	8	6903.796	6	6950.515	6	6897.249	−2	6916.987	2	6864.433	−2			6857.244	9
84	6956.600	6	6903.062	1	6950.567	5	6896.684	2	6916.835	−2	6863.683	1			6856.645	7
85	6956.466	1	6902.322	−0	6950.618	7	6896.108	−2	6916.678	−1	6862.921	2				
86	6956.326	−0	6901.572	−3	6950.672	16	6895.544	10	6916.510	0						
87	6956.171	−6	6900.815	−2	6950.708	11					6861.366	2				
88	6956.022	4	6900.050	−0							6860.569	−2				
89	6955.846	−2	6899.273	−1							6859.769	2				
90	6955.666	−2	6898.486	−1												
91	6955.474	−4	6897.690	−1												
92																
93			6896.067	−2												
94			6895.236	−8												
	^{48}Ti^{35}Cl (2–2)								^{48}Ti^{37}Cl (0–0)							
2	6862.971	5														
3	6863.392	0														
4	6863.810	−4					6859.884	1								
5	6864.234	2					6859.437	8								
6					6862.869	−4										
7	6865.055	−2	6860.055	2	6863.035	−15	6858.512	−1								
8	6865.459	−3	6859.825	1	6863.224	0	6858.049	0					6940.820	7		
9	6865.862	−2	6859.591	−0	6863.392	−3	6857.578	−5					6940.997	1		
10	6866.257	−5	6859.355	0	6863.562	−2	6857.111	−3	6943.611	6			6941.182	4		
11	6866.661	7			6863.729	0	6856.645	3	6943.988	−1			6941.358	2		
12	6867.043	1	6858.869	1	6863.891	0	6856.163	−5	6944.371	2			6941.536	2		
13	6867.427	1	6858.621	3	6864.049	−3	6855.688	−3	6944.745	0			6941.703	−6		
14			6858.363	−1	6864.209	0	6855.208	−3	6945.116	−2			6941.891	9	6933.021	3
15	6868.180	0	6858.105	−0	6864.366	1	6854.728	0	6945.487	1	6935.614	5	6942.051	−2	6932.566	3
16	6868.553	4	6857.840	−2	6864.517	1	6854.240	−3	6945.855	4	6935.356	4	6942.221	−2	6932.109	2
17	6868.908	−6	6857.578	5	6864.668	1	6853.755	−2	6946.219	8	6935.095	5	6942.395	5	6931.646	−2
18	6869.271	−3	6857.300	−1	6864.814	0	6853.265	−1	6946.567	−0	6934.843	18	6942.552	−4	6931.186	−2
19	6869.626	−1	6857.024	1	6864.961	1	6852.774	−0	6946.927	8	6934.555	−1	6942.718	−2	6930.726	0
20	6869.976	−1	6856.739	−2	6865.102	−1	6852.281	1	6947.271	5	6934.283	−0	6942.882	−1	6930.261	−1
21	6870.325	4	6856.452	−0	6865.244	0	6851.781	−3	6947.603	−6	6934.005	0	6943.047	3	6929.798	1
22	6870.661	2	6856.163	3	6865.382	−1	6851.283	−1	6947.952	4	6933.725	1	6943.202	−1	6929.328	−2
23	6870.990	−2	6855.862	−0	6865.521	2	6850.786	2	6948.281	−1	6933.436	−2	6943.358	−2	6928.859	−2
24	6871.317	−2	6855.560	1	6865.654	1	6850.282	1	6948.609	−2	6933.148	1	6943.514	−2	6928.389	−2
25	6871.644	3	6855.254	3	6865.785	0	6849.775	−1	6948.939	3	6932.852	0	6943.672	1	6927.915	−5
26	6871.957	0	6854.939	3	6865.919	3	6849.271	2	6949.255	−0	6932.553	1	6943.825	1	6927.453	5
27	6872.269	3	6854.615	−2	6866.047	3	6848.761	1	6949.564	−6	6932.248	−0	6943.979	3	6926.967	−6
28	6872.571	−0	6854.292	0	6866.177	7	6848.253	4	6949.877	−3	6931.935	−4	6944.124	−3	6926.495	−3
29	6872.869	0	6853.962	1	6866.299	5	6847.739	2	6950.182	−2	6931.620	−5	6944.277	2	6926.022	1
30	6873.162	2	6853.622	−2	6866.422	6	6847.226	4	6950.483	−1	6931.305	−1	6944.421	−2	6925.543	−0
31	6873.453	7	6853.281	−1	6866.546	10			6950.787	10	6930.985	2	6944.568	−1	6925.064	−0

Table 1 (*continued*)

N	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c	Ree	o−c	Pee	o−c	Rff	o−c	Pff	o−c
32	6873.726	1	6852.935	2	6866.661	6	6846.193	6	6951.066	−1	6930.641	−13	6944.712	−2	6924.581	−3
33	6873.995	−2	6852.577	−2	6866.788	17*	6845.678	10	6951.351	2	6930.319	−1	6944.854	−4	6924.102	−0
34	6874.265	0	6852.217	−1	6866.913	27*	6845.158	12	6951.628	1	6929.984	2	6945.002	1	6923.617	−3
35	6874.524	0	6851.847	−4	6867.043	44*	6844.641	18*	6951.900	2	6929.637	−1	6945.137	−4	6923.136	−0
36	6874.777	1	6851.476	−2			6844.119	21*	6952.166	0	6929.285	−3	6945.283	2	6922.652	0
37	6875.023	0	6851.100	2			6843.616	44*	6952.424	−2	6928.928	−5	6945.409	−11	6922.165	−1
38	6875.260	−2	6850.712	0	6867.288	−38*			6952.686	5	6928.575	2	6945.558	1	6921.679	1
39	6875.495	1	6850.319	−0	6867.403	−29*			6952.926	−3	6928.206	−1	6945.699	6	6921.189	−2
40	6875.721	2	6849.922	2	6867.512	−24*	6841.936	−47*	6953.173	1	6927.831	−4	6945.821	−7	6920.699	−3
41	6875.936	−1	6849.514	1			6841.419	−30*	6953.405	−3	6927.453	−4	6945.962	0	6920.214	2
42	6876.143	−5	6849.102	1	6867.723	−15*	6840.896	−20*	6953.634	−4	6927.077	3	6946.100	6	6919.724	3
43	6876.349	−2	6848.681	1	6867.828	−9	6840.364	−16*	6953.856	−6	6926.707	22	6946.220	−5	6919.226	−3
44	6876.545	−1	6848.253	−0	6867.926	−7	6839.831	−11*	6954.080	0	6926.305	15	6946.354	−2	6918.739	3
45	6876.734	−0	6847.818	−2	6868.020	−8	6839.292	−11	6954.288	−3	6925.887	−1	6946.483	−1		
46	6876.916	1	6847.379	1	6868.117	−5	6838.757	−6	6954.500	5	6925.478	−3	6946.610	−2	6917.752	4
47	6877.089	2	6846.930	1	6868.208	−5	6838.209	−12	6954.685	−7	6925.064	−3	6946.735	−3	6917.255	4
48	6877.254	1	6846.472	−1	6868.294	−8	6837.676	−2	6954.885	1	6924.646	−1	6946.863	−0	6916.748	−7
49	6877.412	3	6846.010	1	6868.385	−5	6837.132	−1	6955.080	11	6924.222	1	6946.987	0	6916.269	12
50	6877.558	−0	6845.538	−0	6868.471	−4	6836.580	−6			6923.790	1	6947.110	1	6915.761	4
51	6877.693	−6	6845.062	3	6868.553	−6	6836.034	−4			6923.359	10	6947.231	1	6915.262	4
52	6877.833	2	6844.571	−2	6868.640	−1	6835.484	−5	6955.579	−1	6922.906	3	6947.352	2	6914.752	−5
53	6877.954	−2	6844.077	−2	6868.726	5			6955.739	3	6922.449	−1	6947.471	3	6914.251	−4
54	6878.080	9	6843.577	1	6868.799	−1	6834.388	3	6955.886	1	6921.993	2			6913.752	0
55	6878.179	0	6843.065	−1	6868.877	1	6833.833	2	6956.022	−5	6921.529	3	6947.707	7	6913.248	−0
56	6878.279	2	6842.547	−1			6833.273	−2	6956.171	9	6921.053	1			6912.745	2
57	6878.371	4	6842.021	0	6869.023	1	6832.720	3	6956.283	−6	6920.571	−1	6947.925	−2	6912.238	2
58	6878.452	4	6841.483	−4	6869.092	−1	6832.159	1	6956.411	3	6920.090	4	6948.036	−2		
59	6878.524	3	6840.944	1			6831.601	3	6956.521	1	6919.597	6	6948.149	2	6911.234	14
60	6878.582	−2	6840.394	2			6831.044	9	6956.612	−12	6919.097	7	6948.250	−5	6910.717	7
61	6878.640	2	6839.831	−0	6869.289	−1	6830.478	8	6956.722	1	6918.584	3	6948.363	2	6910.200	1
62	6878.682	−2	6839.265	3	6869.354	2	6829.903	−1	6956.821	12			6948.472	7	6909.682	−5
63	6878.717	−3	6838.686	1	6869.412	1	6829.336	0	6956.890	−0					6909.175	3
64	6878.740	−6	6838.093	−6	6869.471	3	6828.766	0	6956.964	1	6917.012	1			6908.662	5
65	6878.761	−2	6837.506	2	6869.520	−3	6828.202	7	6957.031	3	6916.486	13			6908.132	−9
66	6878.771	−0	6836.902	2	6869.568	−6	6827.624	3			6915.928	1			6907.624	2
67	6878.771	2	6836.288	1	6869.626	3	6827.046	1			6915.370	−3			6907.104	2
68	6878.761	4	6835.664	−1	6869.671	0	6826.463	−4			6914.828	16				
69	6878.740	4	6835.028	−6			6825.887	0			6914.251	8			6906.054	−3
70	6878.717	12	6834.388	−6			6825.310	6			6913.668	2			6905.528	−4
71			6833.743	−0			6824.724	4			6913.073	−8			6905.003	−3
72			6833.082	−2							6912.488	−1			6904.477	−1
73			6832.419	3							6911.886	−2			6903.950	4
74			6831.742	4							6911.284	6			6903.413	−1
75			6831.051	1			6822.358	0			6910.656	−6			6902.878	−2
76			6830.355	2			6821.761	−0			6910.026	−10				
77			6829.645	−0			6821.160	−2								
78			6828.915	−13			6820.554	−4								
79			6828.202	1												
80			6827.460	−3												
81			6826.715	−2												
82			6825.960	1												
83			6825.193	1												

Note. o−c are observed minus calculated wavenumbers in the units of 10^{-3} cm^{-1} and asterisks mark lines affected by a local perturbation in $v = 2$ vibrational level of the upper state, see text for details.

constant H_0' was not well determined and it was therefore fixed to a value estimated using the isotopic relations and the corresponding value for ^{48}Ti^{35}Cl. The rotational line positions for the new transition are provided in Table 1. Rotational analysis indicates that the $v = 2$ vibrational level of the excited state is affected by interactions with a close-lying state near $N = 37$. This interaction affects only one parity level (f-parity) as can be seen from the observed minus calculated differences (Table 1).

The rotational lines were given suitable weights depending on the signal-to-noise ratio and the extent of blending. A number of rotational lines in the vicinity of the perturbation were given lower weights. The

Table 2
Molecular constants (in cm^{-1}) for the new $^2\Sigma$–$^2\Sigma$ system of TiCl

Constants[a]	^{48}Ti^{35}Cl			^{48}Ti^{37}Cl
	0–0	1–1	2–2	0–0
T_{vv}	6938.86489(37)	6900.16900(39)	6861.66625(41)	6939.16086(53)
B'_v	0.1613031(21)	0.1601704(23)	0.1590339(32)	0.1562500(64)
$10^7 \times D'_v$	1.6675(27)	1.6626(36)	1.6579(56)	1.538(12)
$10^{13} \times H'_v$	−2.09(16)	−2.61(24)	−1.41(38)	−1.73[b]
γ'_v	0.21717(18)	0.22875(21)	0.23711(21)	0.20959(43)
$10^5 \times \gamma'_{Dv}$	−2.4638(12)	−2.4745(17)	−2.4446(20)	−2.2552(28)
$10^{10} \times \gamma'_{Hv}$	5.371(14)	5.226(21)	4.680(30)	4.905(45)
B''_v	0.1627121(20)	0.1617505(23)	0.1607852(31)	0.1576438(62)
$10^7 \times D''_v$	1.2478(20)	1.2502(28)	1.2419(48)	1.165(11)
$10^3 \times \gamma''_v$	−4.83(18)	−2.70(20)	−8.0(21)	−4.85(43)

[a] Numbers in parentheses are one standard deviation in the last digits.
[b] Fixed value.

rotational constants obtained for the lower and upper states of Ti^{35}Cl and Ti^{37}Cl are provided in Table 2. The rotational analysis of the new bands indicates that this transition does not have any state in common with the other known electronic states of TiCl [21–23].

In our recent publication on ZrCl [29], we have carried out a comparative ab initio investigation of the changes in the electronic structure in the TiCl, ZrCl, and HfCl series. This work was motivated by the fact that these molecules have different ground states in spite of being isovalent. It is now established that the ground state of TiCl is a $^4\Phi$ state, while ZrCl and HfCl have $^2\Delta$ ground states. In addition to the C$^4\Delta$–X$^4\Phi$, G$^4\Phi$–X$^4\Phi$, and G$^4\Phi$–C$^4\Delta$ quartet transitions, a doublet–doublet transition of TiCl was also identified near 12800 cm^{-1} and was assigned tentatively as [12.8]$^2\Phi$–$a^2\Phi$ but a $^2\Delta$–$a^2\Delta$ assignment is also possible with the lower $^2\Delta$ and $^2\Phi$ states predicted to lie near 3500 and 4500 cm^{-1}, respectively [29]. In addition to the $^2\Delta$ and $^2\Phi$ states, the doublet manifold also has $^2\Sigma^-$ and $^2\Sigma^+$ low-lying states, which are predicted by our ab initio calculations at 5400 cm^{-1} and 7200 cm^{-1}, respectively, above the ground state [29]. A higher lying $^2\Sigma^-$ state has been calculated at 11800 cm^{-1}, predicting a $^2\Sigma^-$–$^2\Sigma^-$ transition at 5441 cm^{-1} consistent with the observed position of the new transition at 6938.9 cm^{-1}. Although a higher lying $^2\Sigma^+$ state was not included in our previous ab initio calculations for TiCl, a $2^2\Sigma^+$ state is also expected to be present near 12000 cm^{-1}. This state of ZrCl was predicted to be at 12600 cm^{-1} by these ab initio calculations [29]. At this moment, therefore, we cannot decide whether the new transition is $^2\Sigma^-$–$^2\Sigma^-$ or $^2\Sigma^+$–$^2\Sigma^+$, since both assignments are possible. The large experimental value of the spin rotation constant γ in the excited state is the result of strong interaction with nearby states. In particular, a nearby $^2\Pi$ state is needed to account for the large spin-rotation constant of 0.217 cm^{-1}. Assuming a simple pure precision interaction [33] with $l = 1$, $\gamma = 4AB/\Delta E$. A reasonable estimate for spin-orbit constant A of the interacting $^2\Pi$ state is 100 cm^{-1}, so the

estimated ΔE is ± 300 cm^{-1}. Also the presence of local perturbations in only one parity level (f-parity) suggests that the perturbing state is a $^2\Pi$ state with substantial Λ-doubling. In the pure precision approximation $p = \gamma = 0.217$ cm^{-1} so a large separation of the Λ-doublets is expected. Our spectra are very complex so no extra lines near the perturbation could be identified with certainty. Although we have not yet identified any TiCl transitions involving a suitable $^2\Pi$ state, a $^2\Pi$ state has been predicted near 12000 cm^{-1} [29].

The rotational constants for the $v = 0$, 1, and 2 vibrational levels (Table 2) have been used in a least squares fit to evaluate the equilibrium constants for the new $^2\Sigma$ states of TiCl (Table 3). The lower state equilibrium constants for Ti^{35}Cl obtained from this fit are $B''_e = 0.1631941(16)$ cm^{-1}, $\alpha''_e = 0.0009632(11)$ cm^{-1}, and $r''_e = 2.260173(11)$ Å while the values of $B'_e = 0.1618707(17)$ cm^{-1}, $\alpha'_e = 0.0011343(12)$ cm^{-1}, and $r'_e = 2.269393(12)$ Å have been determined for the excited $^2\Sigma$ state. We are unable to determine the vibrational intervals in the two $^2\Sigma$ states because of the absence of off-diagonal bands in our spectra. Although we have not been able to determine the equilibrium rotational constants for Ti^{37}Cl, the ratio of the B_0 values of Ti^{35}Cl and Ti^{37}Cl for the lower and upper state yields the values of 1.03215 and 1.03234, respectively, which are in very good agreement with the calculated ratio of the reduced masses of the two isotopomers, $\rho^2 = \mu(\text{Ti}^{37}\text{Cl})/\mu(\text{Ti}^{35}\text{Cl}) = 1.03225$. The value of ρ^2 obtained from the D_0 values of the lower and upper states of the two isotopomers are 1.03493 and 1.04125, respectively, again in good agreement with the calculated value.

Table 3
Equilibrium constants[a] (in cm^{-1}) for the new $^2\Sigma$ states of ^{48}Ti^{35}Cl

Constants	Lower $^2\Sigma$	Upper $^2\Sigma$
B_e	0.1631941(16)	0.1618707(17)
α_e	0.0009632(11)	0.0011343(12)
r_e (Å)	2.260173(11)	2.269393(12)

[a] Values in parentheses are one standard deviation in the last digits.

4. Conclusion

The emission spectrum of TiCl has been recorded in the 4200–8500 cm^{-1} region at a resolution of 0.01 cm^{-1} using a Fourier transform spectrometer. Three bands observed in the 6700–7000 cm^{-1} interval have been assigned as the 0–0, 1–1, and 2–2 bands of a new $^2\Sigma$–$^2\Sigma$ system of TiCl. A rotational analysis has been performed for these bands and spectroscopic constants have been extracted for the new states. The unusually large magnitude of the spin rotation constant for the excited $^2\Sigma$ state, as well as a local perturbation observed in the $v' = 2$ vibrational level is consistent with an interaction with a close-lying $^2\Pi$ state. This work represents the first observation of a $^2\Sigma$–$^2\Sigma$ transition for TiCl.

Acknowledgments

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