

Laser and Fourier transform emission spectroscopy of TaCl

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Abstract

The emission spectrum of TaCl has been recorded at high resolution in the 3000–35000 cm⁻¹ region using a Fourier transform spectrometer. The bands were observed by microwave excitation of a mixture of TaCl₅ vapor and 3.0 Torr of He. Several TaCl bands have also been recorded using the laser ablation/molecular beam source at the University of New Brunswick. A rotational analysis of a number of bands has been obtained and the majority of the stronger bands have been classified into three groups with different lower state spectroscopic constants. The three lower states have been identified as having $\Omega'' = 0^+$, $\Omega'' = 2$, and (tentatively) $\Omega'' = 3$. The $\Omega'' = 0^+$ and $\Omega'' = 2$ states are very close in energy and one of these two states is the ground state of TaCl.
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1. Introduction

Transition metal-containing molecules are species of chemical importance and serve as ideal models for the understanding of bonding and reactivity in transition metal systems [1]. These molecules are also of astrophysical importance. Because of the high abundance of transition metal elements on the surfaces of cool stars, several transition metal-containing diatomic oxides and hydrides have been identified in stellar spectra [2–7] and there is a strong possibility that transition metal halide molecules may also be found. However, precise spectroscopic data are necessary for a search for these species in complex stellar spectra. We have, therefore, initiated a program to study transition metal monohalides by analyzing their high resolution spectra in the visible and near infrared regions.

Like other transition metal halides, very little is known about the electronic structure of TaCl. Only a brief

mention of a few TaCl bands was made in the Ph.D. thesis of Bates [8] which focused on the investigation of the electronic spectra of TaN. In this work, the TaN bands were observed by a microwave excitation of a mixture of TaCl₅ vapor, N₂, and He. However, no attempts were made to obtain electronic, vibrational or rotational assignments of the TaCl bands. Recently we have observed new electronic spectra of the isovalent VCl [9,10] and NbCl [11] molecules. For VCl, we have observed a complex ⁵Δ–⁵Δ transition in the near infrared which was first labeled as the [7.0]⁵Δ–X⁵Δ [9] and later relabeled as the E⁵Δ–X⁵Δ transition [10]. For NbCl we have observed two quintet–quintet transitions in the regions of 6500–7000 cm⁻¹ ($\Delta\Omega = 1$) and 9800–11000 cm⁻¹ ($\Delta\Omega = 0$). Ab initio calculations were also carried out for VCl [10] and NbCl [11] to explain the observed spectra. Ab initio calculations on TaF_n and TaCl_n ($n = 1–5$) have been carried out by Bauschlicher [12] to predict the spectroscopic properties of the low-lying states. For TaCl one of two very close-lying states with $\Omega = 0^+$ or $\Omega = 2$ was predicted to be the ground state. According to this calculation, there is a very small separation of only 110 cm⁻¹ between these

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two lower states. This theoretical work was centered only on the study of very low-lying electronic states of TaCl [12] and no predictions were made for higher-lying states that are responsible for the TaCl spectra in the visible and near infrared regions.

In the present work, we report on our investigation of TaCl spectra using laser ablation/molecular beam spectroscopy and Fourier Transform (FT) emission spectroscopy. A rotational analysis of a number of bands has been obtained and spectroscopic constants have been determined. Based on the rotational analysis, the majority of observed TaCl bands have been classified into three groups with different lower states $\Omega'' = 0$, $\Omega'' = 2$, and $\Omega'' = 3$. The observation of these low-lying states of TaCl is supported by the available theoretical calculations on TaCl [12] and TaH [13]. To identify the ground state of TaCl we looked at the effect of the backing pressure on the relative intensity of two transitions using the laser ablation spectrometer. The results were inconclusive and it was not possible for us to decide whether the ground state has $\Omega'' = 0$ or $\Omega'' = 2$.

2. Experimental

2.1. Fourier transform emission spectroscopy

The TaCl molecules were excited in a microwave discharge through a flowing mixture of about 3.0 Torr of helium and a trace of TaCl₅ vapor, which was generated by controlled heating of TaCl₅ powder placed in a small bulb attached to the discharge cell. The spectra were recorded using the 1-m Fourier transform spectrometer associated with the McMath-Pierce Telescope of the National Solar Observatory at Kitt Peak. The spectra in the 3000–35 000 cm⁻¹ region were recorded in three parts. The spectra in the 3000–15 000 cm⁻¹ region were recorded using liquid nitrogen-cooled InSb detectors and a RG695 filter. The spectrometer was equipped with a CaF₂ beamsplitter. A total of 5 scans were co-added in about 40 minutes of integration at a resolution of 0.02 cm⁻¹. The spectrum in the 9500–19 000 cm⁻¹ region was recorded using midrange Si-diode detectors and a GG495 filter at a resolution of 0.025 cm⁻¹. This time six scans were co-added in about 50 min of integration. Lastly the spectra in the 17 500–35 000 cm⁻¹ region were recorded using midrange Si-diode detectors and a CuSO₄ filter by co-adding nine scans at a resolution of 0.025 cm⁻¹. For the visible and near UV scans the spectrometer was equipped with a quartz UV beamsplitter.

The spectral line positions were measured using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each line. The FT spectra were calibrated using the measurements of common TaCl molecular lines in the FT spectra and in the

laser ablation/molecular beam spectra recorded at the University of New Brunswick. The molecular lines typically appear with a width of 0.032 cm⁻¹ and a signal-to-noise ratio of about 7:1 for the strong bands observed in the FTS spectra. The line positions are expected to be accurate to about ± 0.003 cm⁻¹ for the strong bands although the measurement uncertainty for blended and weak lines is expected to be somewhat higher.

2.2. Laser excitation spectroscopy

The apparatus used to create the TaCl molecule in the molecular beam work has been described previously [14,15], however, some details pertinent to this work will be given. A tantalum target in the form of a slowly rotating and translating rod mounted near the opening of a pulsed molecular beam valve (General Valve Series 9) was ablated by about 4 mJ of 355 nm radiation from a Nd:YAG laser. At the same time, an optimum gas mixture of 1% CCl₄ seeded in helium was passed through the valve into the ablation region. Vaporized tantalum was entrained in the gas mixture and then expanded through a short expansion channel into the vacuum system producing a molecular jet.

TaCl molecules were formed through the reaction of the hot Ta atoms with CCl₄ and its decomposition products during the expansion process. About 5 cm downstream from the expansion orifice, the molecules were probed with a tunable dye laser. For low-resolution studies a Lumonics pulsed dye laser was used, while for high resolution studies, the laser was a Coherent 699-29 “Autoscan” c.w. ring dye laser. Laser-induced fluorescence was collected orthogonally to both the molecular beam and the probe laser and imaged on to a 0.25 m monochromator. Light passing through the monochromator was detected by a cooled photomultiplier tube. The signal was amplified, integrated using a boxcar integrator, and sent to a PC controlling the laser system. To record the spectra of the green system of TaCl (17 990 cm⁻¹), the dye C540A was used in the pulsed laser while R110 was used in the ring laser. For the red system (15 684 cm⁻¹), DCM dye was used in the pulsed laser and Kiton Red was used in the ring laser. As the pulsed studies were used mainly to optimize the production of TaCl and to see if increasing the stagnation pressure through the pulsed valve would increase the intensity of one band over the other, no effort was made to calibrate the spectra. However, for the data taken with the ring laser, the line positions were measured with the “Autoscan” system which has a specified absolute frequency accuracy of ± 200 MHz and a precision of ± 60 MHz. Calibration of the “Autoscan” system was maintained by recording the I₂ spectrum and comparing the line positions with the values in the I₂ atlas [16].

The high resolution data were difficult to collect as the fluorescence signals were quite weak. These weak

signals were also lying on a large plasma background signal arising from the ablation source and this background signal could not be totally eliminated using the monochromator. In some instances, several scans taken using long time constants on the boxcar integrator were co-added in an attempt to increase the S/N ratio. In particular, this method was used when trying to record the much weaker low J lines which are critical to getting the rotational assignment of the band correct. Typical linewidths of the high resolution data were about 225 MHz; the co-added linewidths were larger by about a factor of two.

3. Theoretical background

Although there are no previous experimental studies available for Ta containing halides, some theoretical calculations have been reported for the related molecules VCl [10], NbCl [11], and TaH [13], and more recently for TaF and TaCl [12]. Our theoretical calculations on VCl [10] and NbCl [11] have predicted a $^5\Delta$ ground state although a more recent calculation on VF by Koukounas et al. [17] has suggested a $^5\Pi$ state as a better candidate for the ground state. For TaH, Cheng and Balasubramanian [13] have included spin–orbit effects in their ab initio calculations. They have concluded that almost all the electronic states of TaH are heavy mixtures of different λ -s states tending towards an intermediate Hund's coupling case. The ground state of TaH was predicted to be $\Omega = 0^+$ state followed by a $\Omega = 2$ state lying somewhat higher in energy. The results of these calculations were helpful in our electronic assignment of the observed TaCl bands.

Without taking into account the effects of spin–orbit coupling, Bauschlicher [12] has predicted a $^3\Sigma^-$ state as the lowest followed by a $^3\Phi$ state. After taking into account spin–orbit effects, Bauschlicher [12] found that the $\Omega'' = 2$ state was the lowest with $\Omega'' = 0^+$ lying at 435 cm^{-1} above the $\Omega'' = 2$ state. Both of these states are derived from triplet states ($^3\Sigma_0^-$ and $^3\Phi_2$) but other states also make a contribution. The inclusion of quintet states $^5\Sigma^+$, $^5\Delta$, $^5\Pi$, and $^5\Phi$ states along with these low-lying $^3\Sigma^-$ and $^3\Phi$ states in the calculation lowered the separation between the $\Omega'' = 0^+$ and $\Omega'' = 2$ states to 110 cm^{-1} with $\Omega'' = 2$ still being the lowest. This separation is too small (and within the uncertainty of the theoretical results) to draw any firm conclusion about which of the two is really the lowest. Although Bauschlicher [12] did not attempt to predict the nature of the higher-lying states, the excited states of TaCl are also most likely mixtures of several states. Therefore, at this stage it is difficult to make any Hund's case (a) electronic assignment for the excited states observed experimentally. We will, therefore, label the excited states only with their assigned Ω values.

4. Observations

Our spectra contain a number of new TaCl bands in the $5000\text{--}18800\text{ cm}^{-1}$ region, in addition to the four bands observed by Bates [8] at 17990 , 17830 , 17600 , and 17570 cm^{-1} . The $19000\text{--}35000\text{ cm}^{-1}$ region is free from any TaCl bands although some TaO bands were observed strongly to higher wavenumbers. TaCl bands were distinguished from TaO bands based on the smaller line spacing in the TaCl branches. Most of the strong TaCl bands observed in the FT spectra have been rotationally analyzed. In some strong bands the rotational lines of the Ta ^{37}Cl isotopologue were also observed, establishing the carrier of the new bands as TaCl. After rotational analysis, these bands have been divided into three groups with different lower state rotational constants, although the lower state vibrational intervals are similar in magnitude. The three lower states have tentatively been assigned as $\Omega = 0^+$, $\Omega = 2$, and $\Omega = 3$, supported by the theoretical calculation of Bauschlicher [12]. Several additional bands were observed in the laser ablation/molecular beam spectrum, a number of which have been assigned as higher vibrational bands of transitions in the three groups. A number of bands in the laser ablation/molecular spectrum could not be accommodated in these three groups and probably belong to additional transitions. The assignment of these bands could not be made because of the lack of high resolution spectra. The observed TaCl bands over the entire range have been listed in Table 1 and our proposed assignments have also been provided.

The rotational lines of the TaCl bands were sorted using a color Loomis–Wood program running on a PC computer. This program was very helpful in identifying the lines particularly in the weaker and overlapped bands. The rotational analysis of bands in the three groups was obtained by comparing the combination differences for the common vibrational levels. The molecular constants were determined by fitting the observed line positions with the customary energy level expressions:

(for $\Omega = 0^+$ and higher Ω states)

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 \quad (1)$$

(for $\Omega = 1$ states)

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 \\ \pm 1/2 \{ q_v J(J+1) + q_{Dv} (J(J+1))^2 \\ + q_{Hv} (J(J+1))^3 \}. \quad (2)$$

Blended and weaker lines were given reduced weights and badly overlapped lines were excluded to improve the standard deviation of the fits. The rotational constants for the observed states were determined by fitting

Table 1
Observed band heads of TaCl in the 5000–18 800 cm⁻¹ region

λ_{air}^a (nm)	ν_{vac} (cm ⁻¹)		Remarks
<i>Group I</i>			
622.266	16062.7116*	b,c	1–0 band 15 684 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
637.234	15683.7761*	b,c	0–0 band 15 684 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
637.345	15681.7476*	b,c	0–0 band 15 684 cm ⁻¹ system of Ta ³⁷ Cl, rotationally analyzed
637.935	15667.4443*	c	1–1 band 15 684 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
688.514	14517.5898*	b,c	1–0 band 14 178 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
688.651	14517.13	b,c	1–0 band 14 178 cm ⁻¹ system of Ta ³⁷ Cl, no analysis
704.979	14178.1800*	b	0–0 band 14 178 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
725.381	13782.9127*	c	0–1 band 14 178 cm ⁻¹ system of Ta ³⁵ Cl, rotationally analyzed
<i>Group II</i>			
534.041	18719.95	b	2–0 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis,
544.573	18357.92	b	1–0 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
555.580	17989.8885*	b,c	0–0 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
556.537	17968.25	b	1–1 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
568.009	17595.4129*	b,c	0–1 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
568.927	17567.1963*	b,c	1–2 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
569.903	17538.8545*	b,c	2–3 band 17 990 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
538.301	18571.83	b	2–0 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
539.285	18537.92	b	3–1 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
549.087	18202.4963*	b,c	1–0 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
549.977	18172.9768*	b,c	2–1 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
551.109	18141.1439*	b,c	3–2 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
560.474	17832.6697*	b,c	0–0 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
573.143	17442.82	b	0–1 band 17 833 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
577.261	17318.41	b	1–0 band 16 964 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
589.144	16963.7339*	b,c	0–0 band 16 964 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
679.832	14705.46	b	2–0 band 13 978 cm ⁻¹ transition of Ta ³⁵ Cl, no analysis
696.921	14344.87	b	1–0 band 13 978 cm ⁻¹ transition, no rotational analysis
715.105	13977.5703*	b,c	0–0 band 13 978 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
760.036	13155.2058*	c	0–0 band 13 155 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
764.501	13076.3424*	c	0–0 band 13 076 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
<i>Group III</i>			
602.605	16588.1692*	c	1–0 band 16 243 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
615.411	16242.8451*	c	0–0 band 16 243 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
753.668	13265.5119*	c	0–0 band 13 266 cm ⁻¹ transition of Ta ³⁵ Cl, rotationally analyzed
1727.876	5784.1445*	c	A transition between two excited states (see Fig. 3), Rot. structure analyzed
<i>Isolated and unassigned bands</i>			
532.764	18764.82	b	2–0 band 18 039 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
543.228	18403.39	b	1–0 band 18 039 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
554.200	18039.05	b	0–0 band 18 039 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
566.432	17649.50	b	0–1 band 18 039 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
675.480	14800.21	b	1–0 band 14 466 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
691.041	14466.94	b	0–0 band 14 466 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
691.197	14463.66	b	0–0 band 14 466 cm ⁻¹ transition of Ta ³⁷ Cl, no rotational analysis
680.368	14693.87	b	1–0 band 14 322 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
698.008	14322.54	b	0–0 band 14 322 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
699.141	14299.34	b	1–1 band 14 322 cm ⁻¹ transition of Ta ³⁵ Cl, no rotational analysis
538.860	18552.53	b	No analysis
540.174	18507.42	b	No analysis
544.856	18348.38	b	No analysis
546.078	18307.34	b	No analysis
549.352	18197.88	b	No analysis
559.287	17872.4375*	c	Rotational structure analyzed
575.608	17368.13	b	No analysis
577.599	17308.27	b	No analysis
588.453	16986.40	b	No analysis
690.950	16914.9358*	c	Rotational structure analyzed
606.350	16481.4739*	c	Rotational structure analyzed
650.206	15375.52	b	No analysis
654.538	15273.75	b	No analysis
678.063	14743.83	b	No analysis

^a Wavelengths are the *R* head positions (in nm) measured from the low resolution laser ablation or FT spectra. The letters “b” and “c” refer bands observed in the laser ablation and the FT experiments, respectively, while asterisks mark the origins of the rotationally analyzed bands.

Table 2
Spectroscopic constants (in cm^{-1}) for the observed states of TaCl

Constants	$X_1 \Omega = 0^+, v = 0$	$X_1 \Omega = 0^+, v = 1$	$[14178] \Omega = 0^+, v = 0$	$[14178] \Omega = 0^+, v = 1$	$[15686] \Omega = 0^+, v = 0$	$[15686] \Omega = 0^+, v = 1$
(A) Constants for states in group I						
T_v	a	$a + 395.2673(11)$	$a + 14178.17997(66)$	$a + 14517.5898(53)$	$a + 15683.77609(65)$	$a + 16062.7116(12)$
B_v	0.1147761(27)	0.1143241(28)	0.1100758(27)	0.1095049(47)	0.1099967(27)	0.1092025(28)
$10^8 \times D_v$	3.901(17)	3.954(18)	4.705(16)	4.688(62)	3.321(17)	3.136(18)
Constants	$X_2 \Omega = 2, v = 0$	$X_2 \Omega = 2, v = 1$	$X_2 \Omega = 2, v = 2$	$X_2 \Omega = 2, v = 3$		
(B) Constants for states in group II						
T_v	b	$b + 394.4756(14)$	$b + 786.00^*$	$b + 1173.00^*$		
B_v	0.1134527(37)	0.1130128(38)	0.1125564(81)	0.1121720(26)		
$10^8 \times D_v$	3.685(37)	3.730(39)	3.504(94)	4.096(36)		
	$[13076] \Omega = 2, v = 0$	$[13155] \Omega = 1, v = 0$	$[13978] \Omega = 3, v = 0$	$[16964] \Omega = 2, v = 0$		
T_v	$b + 13076.3424(27)$	$b + 13155.2058(95)$	$b + 13977.5703(14)$	$b + 16963.7339(10)$		
B_v	0.1103915(43)	0.1075171(38)	0.1083648(37)	0.1092517(36)		
$10^8 \times D_v$	2.921(65)	3.944(38)	3.569(37)	3.978(36)		
$10^{13} \times H_v$	-5.44(34)	—	—	—		
$10^9 \times q_{Dv}$	—	1.85(13)	—	—		
$10^{13} \times q_{Hv}$	—	-1.00(14)	—	—		
	$[17833] \Omega = 2, v = 0$	$[17833] \Omega = 2, v = 1$	$[17833] \Omega = 2, v = 2$	$[17833] \Omega = 2, v = 3$		
T_v	$b + 17832.6697(13)$	$b + 18202.4963(20)$	$b + 18567.4524(27)$	$b + 18927.1439(14)$		
B_v	0.1085129(38)	0.1084279(51)	0.1078856(52)	0.1073591(79)		
$10^8 \times D_v$	2.884(41)	-9.25(15)	1.43(13)	1.431(92)		
	$[17990] \Omega = 2, v = 0$	$[17990] \Omega = 2, v = 1$	$[17990] \Omega = 2, v = 2$	—		
T_v	$b + 17989.88854(81)$	$b + 18353.1963(22)$	$b + 18711.8545(34)$	—		
B_v	0.1090667(38)	0.1083406(82)	0.108313(25)	—		
$10^8 \times D_v$	3.285(44)	-1.13(12)	4.41(35)	—		
$10^{12} \times H_v$	-0.604(23)	-2.393(54)	—	—		
Constants	$X_3 \Omega = 3?, v = 0$	$[7481] \Omega = 2?, v = 0$	$[13266] \Omega = 2?, v = 0$	$[16243] \Omega = 3?, v = 0$	$[16243] \Omega = 3?, v = 1$	
(C) Constants for states in group III						
T_v	c	$c + 7481.4375(21)$	$c + 13265.5195(75)$	$c + 16242.8451(10)$	$c + 16588.1692(16)$	
B_v	0.1142102(53)	0.1135927(55)	0.1099379(52)	0.1081028(52)	0.1076229(54)	
$10^8 \times D_v$	4.004(56)	4.201(59)	3.949(54)	4.320(55)	4.344(64)	
Constants	$16481 \text{ cm}^{-1}, \Delta\Omega = 0$	$16915 \text{ cm}^{-1}, \Delta\Omega = 0$	$17872 \text{ cm}^{-1}, \Delta\Omega = 0$			
(D) Constants for bands with uncertain assignments						
T_{vv}	16481.4739(18)	16914.9358(14)	17872.4375(12)			
B'_v	0.107962(20)	0.1084833(54)	0.1087960(55)			
$10^8 \times D'_v$	3.06(34)	4.071(41)	4.490(44)			
B''_v	0.112776(21)	0.1137375(54)	0.1137375(54)			
$10^8 \times D''_v$	2.63(36)	3.784(42)	3.784(42)			

Note. The letters “a,” “b,” and “c” represent the unknown term energies of X_1 , X_2 , and X_3 lower states, respectively. One of the X_1 and X_2 states is the ground state of TaCl. The values in parentheses are one standard deviation in the last digits quoted. Asterisks mark fixed values based on extrapolation.

the rotational lines of bands in the three groups separately. The line positions in the bands of the three groups may be obtained from the authors upon request or from the supplementary data available on line [18]. The spectroscopic constants obtained for the bands in the three groups have been provided in Table 2. A description of bands in each group will be provided in the following sections, with the transitions labeled by their 0–0 band positions.

4.1. Group I, lower state $\Omega'' = 0^+$

Two transitions with 0–0 bands near 14178 and 15684 cm^{-1} have a common lower state and the bands belonging to these two transitions have been collected in group I. A schematic diagram of group I is provided in Fig. 1. Three bands located near 13783, 14178, and

14518 cm^{-1} have been assigned as the 0–1, 0–0, and 1–0 bands of the lower wavenumber transition (14178 cm^{-1} system) and the bands located near 15668, 15684, and 16063 cm^{-1} have been assigned as the 1–1, 0–0 and 1–0 bands of the higher wavenumber transition (15684 cm^{-1} system). The high resolution spectrum of all of these bands were observed in our FT spectra. The 0–1 band of the 15684 cm^{-1} transition was absent in our FT spectra because of its weak intensity. The observation of the 1–1 and 1–0 bands of this transition, however, establishes the assignment of this transition. No higher vibrational bands of the two transitions were observed in our spectra, and therefore the equilibrium vibrational constants could not be obtained for the observed states. These transitions are also present in our low resolution laser scans although only the 15684 cm^{-1} band was recorded in the high

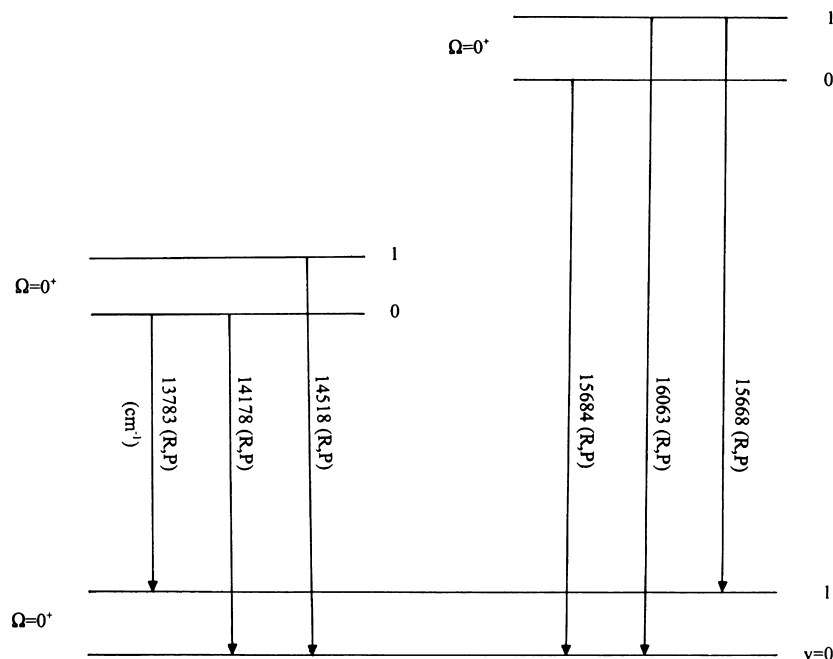


Fig. 1. A schematic energy level diagram for TaCl bands with $X_1 \Omega = 0^+$ as the common lower state.

resolution laser ablation/molecular beam experiments. The rotational lines of the minor isotopomer Ta³⁷Cl were also measured for the 0–0 band in our FTS and laser spectra and constants were determined by rotational analysis. The rotational structure of these bands consists of a single *R* and a single *P* branch without any doubling, consistent with the $\Delta\Omega = 0$ assignment with $\Omega' = \Omega'' = 0^+$. Although the lowest *R* and *P* lines could not be assigned with certainty because of overlapping of low *J* lines by returning lines of the *R* branch after the formation of the band head, this assignment is consistent with ab initio predictions of Bauschlicher [12]. A part of the 15684 cm⁻¹ band from the FT and laser ablation spectra has been provided for comparison in Fig. 2. A weak head belonging to the Ta³⁷Cl 0–0 band has also been marked in Fig. 2.

4.2. Group II, lower state $\Omega'' = 2$

Twelve TaCl bands, classified into six electronic transitions have a common lower state and have been collected into group II (Fig. 3). The 0–0 bands of the transitions in this group are located near 13076, 13155, 13978, 16964, 17833, and 17990 cm⁻¹. Four bands with band origins near 13076, 13155, 13978, and 16964 cm⁻¹ have been identified as 0–0 bands of four different transitions having their lower state in common. Out of these, the 13076 and 16964 cm⁻¹ transitions have only one *R* and one *P* branch each suggesting that they involve a $\Delta\Omega = 0$ transition. The 13155 cm⁻¹ transition has *R*, *P*, and *Q* branches which are split into two components at higher *J* values whereas

the 13978 cm⁻¹ transition has a single *R*, a single *P*, and a single *Q* branch. These two transitions have $\Delta\Omega = 1$ with Ω' and $\Omega'' \geq 1$. Rotational analysis of these transitions with same lower state indicates that there is no Ω -doubling in the common lower state, and the doubling observed in the 13155 cm⁻¹ transition arises due to Ω -doubling in the excited state. From these observations we have concluded that the common lower state of this group is an $\Omega = 2$ state. The upper state of the 13076 cm⁻¹ transition is therefore an $\Omega = 2$ state. The upper state of the 13155 cm⁻¹ transition which has very small Ω -doubling in the excited state can be assigned as an $\Omega = 1$ state. An $\Omega = 3$ assignment is also equally possible if the observed Ω -doubling is a result of the onset of a parity selective perturbation around *J* = 60. The upper state of the 13978 cm⁻¹ transition, which has *R*, *P*, and *Q* branches without Ω -doubling, can be assigned as an $\Omega = 3$ state. The upper state of the $\Delta\Omega = 0$ transition near 16964 cm⁻¹ is an $\Omega = 2$ state. No higher vibrational bands with *v* > 0 were observed for the 13076, 13155, 13978, and 16964 cm⁻¹ transitions.

The next two higher wavenumber transitions have their 0–0 bands with origins near 17833 and 17990 cm⁻¹. Both of these transitions have single *R* and a single *P* branches without any splitting so were assigned as $\Omega = 2$ states. For these transitions several excited vibrational bands were identified in our FT and laser spectra. For the 17833 cm⁻¹ transition we have identified the 2–0, 3–1, 1–0, 2–1, 3–2, 0–0, and 0–1 bands, and rotational analyses were carried out for the 0–1, 1–0, 2–1, and 3–2 bands using the measurements from our Fourier trans-

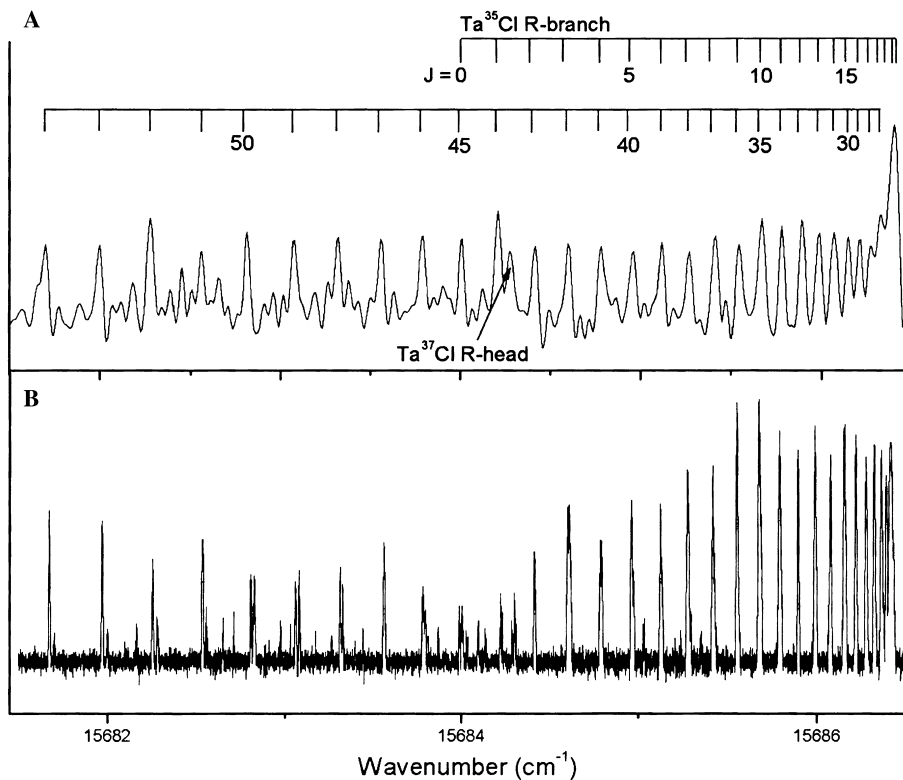


Fig. 2. A portion of the spectrum of the 15684 cm^{-1} band near the *R* head. The FTS and laser ablation/molecular beam spectra have both been provided for comparison.

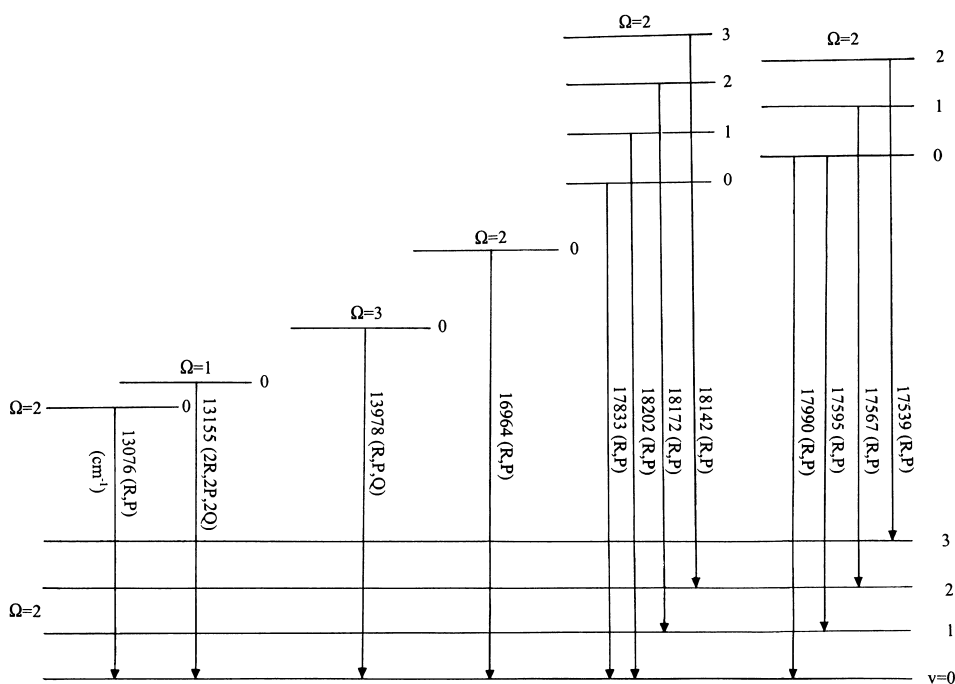


Fig. 3. A schematic energy level diagram for TaCl bands with $X_2 \Omega = 2$ as the common lower state.

form spectra. The assignment of the 2–1 and 3–2 bands in our Fourier transform spectra was supported by the observation of 2–0 and 3–1 bands in our low resolution laser ablation spectra.

For the 17990 cm^{-1} transition we have obtained rotational analyses of the 0–1, 0–0, 1–2, and 2–3 bands using our measurements from the Fourier transform spectra. The 17990 cm^{-1} transition has also been

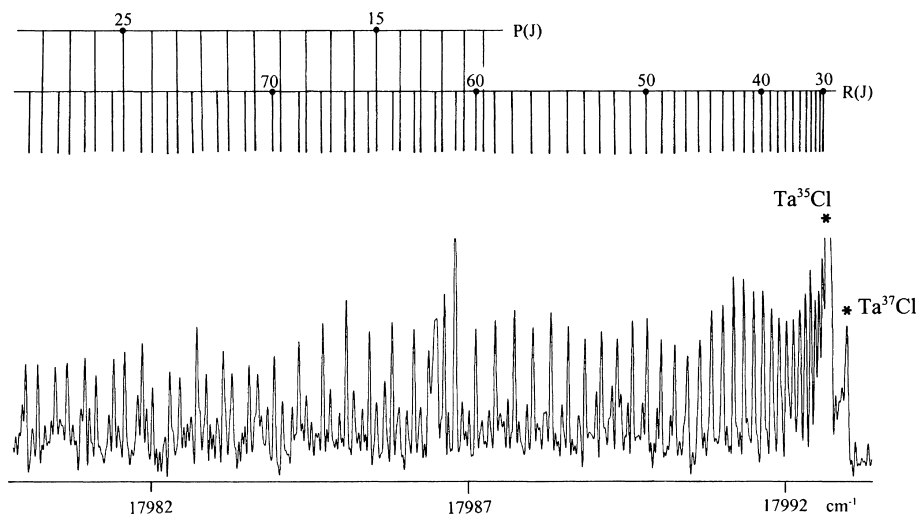


Fig. 4. An expanded portion of the FTS spectrum of the 17990 cm^{-1} band near the R head.

measured at high resolution using the laser ablation spectra. The measurements of low J lines of the 17990 cm^{-1} band from the laser spectra were also included in the analysis of this band. Again the vibrational assignment of the 1–2 and 2–3 bands of this transition was supported by the observation of 1–1, 1–0, and 2–0 bands in our laser ablation/molecular beam spectra. The rotational assignment in the bands involving the $v'' = 1$ and 2 vibrational levels of the lower $\Omega'' = 2$ state was obtained by comparing the lower state combination differences from bands with a common lower state in the 17833 and 17990 cm^{-1} transitions. A part of the spectrum of the 0–0 band at 17990 cm^{-1} has been presented in Fig. 4, in which some R and P lines have been marked. No attempt was made to obtain a rotational analysis of this band for the Ta^{37}Cl isotopologue which was weakly present in our spectra.

4.3. Group III, lower state $\Omega'' = 3?$

Four bands having an upper or lower state in common have tentatively been identified into another group which has been labeled as group III (Fig. 5). Two widely separated bands with origins near 13266 and 16243 cm^{-1} have been assigned the 0–0 bands of two different transitions. For the 13266 cm^{-1} transition only the 0–0 band has been rotationally analyzed. This band has a single R , a single P , and a single Q branch without any splitting, suggesting a $\Delta\Omega = 1$ transition with $\Omega > 1$. The 16243 cm^{-1} transition has only R and P branches without any doubling suggesting a $\Delta\Omega = 0$ transition with $\Omega > 1$. Another band with an origin near 16588 cm^{-1} has been identified as the 1–0 band of the 16243 cm^{-1} transition. The third transition is located in the near infrared near 5784 cm^{-1} . This transition has an upper state in common with the 0–0 band near 13266 cm^{-1} . On the basis

of the observed rotational structure and absence of any Ω -doubling in any of these bands we have tentatively given an assignment of $\Omega'' = 3$ for the common lower state of group III. This assignment is very tentative since R and P branches in the bands involving this state have very similar intensities. The absence of Ω -doubling in the 13266 cm^{-1} bands leads us to assign the excited state of this transition as a $\Omega = 2$ state. The lower state of the 5785 cm^{-1} transition, therefore, is also an $\Omega = 2$ state. The 16243 cm^{-1} transition with a single R and a single P branches can then be assigned as an $\Omega = 3$ state.

It has to be stressed that none of the bands collected in group III were observed in the laser ablation/molecular beam spectra, suggesting that $\Omega'' = 3$ state is probably considerably higher in energy than the $\Omega'' = 0^+$ and $\Omega'' = 2$ states of group I and II. The $\Omega'' = 3$ lower state probably arises from the low-lying $^3\Phi$ state. The lower state vibrational interval for this state could not be measured directly because of the absence of the 0–1 band in any of the observed transitions.

4.4. Other isolated and unassigned bands

Although most of the bands observed in our FT spectra were rotationally analyzed, a number of bands observed in laser ablation/molecular beam spectra could not be analyzed because of the lack of high resolution spectra. Attempts were made to obtain a vibrational assignment of these bands based on known lower state vibrational intervals of the bands in the three groups. A number of these bands have tentatively been assigned into three different transitions based on the lower state vibrational intervals and the observed $\text{Ta}^{35}\text{Cl}/\text{Ta}^{37}\text{Cl}$ isotopic shifts.

Four bands with R heads at 17649.50 , 18039.05 , 18403.39 , and 18764.82 cm^{-1} have tentatively been

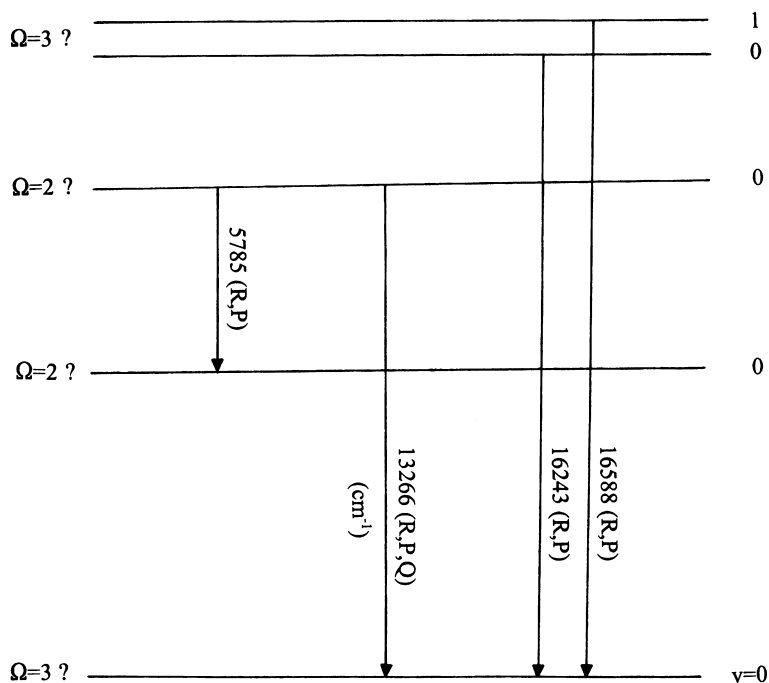


Fig. 5. A schematic energy level diagram for TaCl bands with $X_3 \Omega = 3$ as the common lower state.

assigned as the 0–1, 0–0, 1–0, and 2–0 bands of a new transition which we will call as “18039 cm^{-1} transition.” This assignment provides $\Delta G''_{1/2} = 389.55$, $\Delta G'_{1/2} = 364.34$, and $\Delta G'_{3/2} = 361.43 \text{ cm}^{-1}$ for this transition. Although the Ta³⁵Cl/Ta³⁷Cl isotopic heads were not clearly identified, these bands seem to belong to a separate transition since these bands could not be accommodated into the transitions of the three known groups. None of these bands were observed in our FTS spectra.

Two bands located at 14466.94 and 14800.21 cm^{-1} have tentatively been assigned as the 0–0 and 1–0 bands of a separate transition. The 0–1 band of this transition is not present in our spectra although a weaker head located at 14463.66 cm^{-1} can be assigned as the 0–0 band of the Ta³⁷Cl isotopomer providing a large Ta³⁵Cl/Ta³⁷Cl isotope shift of 3.28 cm^{-1} for the 0–0 band. We have labelled this transition as the “14466 cm^{-1} transition.”

To lower wavenumbers, the three bands located at 14299.34, 14322.54, and 14693.87 cm^{-1} have been tentatively assigned as the 1–1, 0–0, and 1–0 bands of another transition labeled as the “14322 cm^{-1} transition.” The 0–1 band of this transition has not been identified, although the assignment of the 14299.34 cm^{-1} band as the 1–1 band provides $\Delta G''_{1/2} = 394.54$ and $\Delta G'_{1/2} = 371.34 \text{ cm}^{-1}$.

Three bands with origins near 16481, 16915, and 17872 cm^{-1} were found to be present only in our FT spectra and their rotational analysis has also been performed. The 16915 and 17872 cm^{-1} bands have their lower state in common but this lower state does not match any vibrational levels of the transitions in the

three groups. It is possible that these bands involve higher vibrational levels of one of the three lower states. The vibrational assignment of these bands could not be made under the present circumstances. The lower and upper state constants of the 16481 cm^{-1} band do not match with the constants of any of the known states. The vibrational and electronic assignment of this band is completely uncertain. The spectroscopic constants obtained from the analysis of these three bands have also been provided in Table 2.

5. Discussion

Although the lower state vibrational interval was not measured for the bands in group III ($\Omega'' = 3$), the lower states of group I ($\Omega'' = 0^+$) and II ($\Omega'' = 2$) have vibrational intervals of similar magnitude (see Table 2). As has been pointed out by Bauschlicher [12], the $\Omega'' = 0^+$ and $\Omega'' = 2$ states lie very close in energy and the ground state of TaCl is one of the two states. Bauschlicher [12] has concluded that the $\Omega'' = 0^+$ and $\Omega'' = 2$ states are mixtures of low-lying triplet and quintet states with main contribution coming from the low-lying $^3\Sigma^-$ and $^3\Phi$ states. According to Bauschlicher's results [12], the $^3\Sigma^-$ and $^3\Phi$ states of TaCl have vibrational constants of 401 and 388 cm^{-1} , respectively, in good agreement with our observed vibrational interval of $\Delta G_{1/2} = 395 \text{ cm}^{-1}$. The spectroscopic constants for the states for which two or more vibrational bands were observed (Table 2) have been used to determine the equilibrium constants which are listed in

Table 3
Equilibrium constants (in cm^{-1}) for the electronic states of TaCl

State	ω_e	$\omega_e x_e$	B_e	α_e	r_e (Å)
$X_1 \Omega = 0^+$	[395.2673(11)] ^a	—	0.1150021(33)	0.0004520(39)	2.236511(32)
$X_2 \Omega = 2$	398.50(71)	1.86(17)	0.113659(15)	0.0004258(56)	2.24969(15)
[14178] $\Omega = 0^+$	[339.4098(17)] ^a	—	0.1103712(38)	0.0005709(54)	2.282948(39)
[15684] $\Omega = 0^+$	[378.9355(13)] ^a	—	0.1103938(33)	0.0007942(39)	2.282715(34)
[17833] $\Omega = 2$	374.93(14)	2.52(36)	0.10876(15)	0.0003537(82)	2.2998(16)
[17990] $\Omega = 2$	367.9576(51)	2.3248(23)	0.10936(15)	0.00062(18)	2.2935(16)

^a $\Delta G_{1/2}$ values.

Table 3. The equilibrium constants for the [17833] and [17990] states were not very well determined because of a small irregularity in the vibrational intervals and rotational constants with increasing v values. We have been unable to determine the relative positions of the low-lying electronic states because of the lack of cross-transitions between the states of group I and group II.

The identification of the ground state of TaCl is particularly difficult since both these states were observed in the laser ablation/molecular beam spectra recorded at University of New Brunswick. To obtain additional information on the nature of the ground state, two bands, one at 15684 cm^{-1} (group I) and the other at 17990 cm^{-1} (group II), were chosen for detailed study. These two bands were recorded at high resolution in the laser ablation/molecular beam source but that did not help in deciding the nature of the ground state. A study was, therefore, undertaken to see if either of the bands was reduced in relative intensity if the backing pressure of the molecular jet source was increased. Increasing the source pressure should have the effect of reducing the relative intensity of the higher-lying state. Unfortunately, within the limitations of the UNB source, the relative intensity of the two bands was unchanged as the pressure was increased. Both states increased to a certain level and remained at that intensity as the highest source pressure of about 6.5 atm was reached. This test therefore proved inconclusive except to indicate that the two states are both very close and low-lying in energy.

The actual Ω assignment of the bands also proved difficult to determine. This should have been straight forward given the observation of the first lines in the spectrum. Unfortunately the low- J lines were quite weak in both bands. In addition, the low- J R -lines were also obscured by more intense returning R -lines from the band heads. Much effort was taken to improve the signal-to-noise ratio of these weak lines. Eventually, this resulted in several scans of the same frequency region being averaged together and some weak lines were picked out of the noise. The green system was eventually identified as an $\Omega' = 0 - \Omega'' = 0$ transition while the red system was identified as an $\Omega' = 2 - \Omega'' = 2$ transition.

As mentioned earlier, a relatively large isotope splitting was observed in the 0–0 band of the 15684 cm^{-1} transition. We have carried out a rotational analysis of both Ta^{35}Cl and Ta^{37}Cl for the 0–0 band at 15684 cm^{-1} . The rotational constants obtained from the 0–0 band of Ta^{37}Cl are $T_{00} = 15681.74993(56)$, $B' = 0.1051073(76)$, and $B'' = 0.1096163(78) \text{ cm}^{-1}$, while the corresponding values for the main isotopologue Ta^{35}Cl are $T_{00} = 15683.77609(65)$, $B' = 0.1099967(27)$, and $B'' = 0.1147761(27) \text{ cm}^{-1}$. These constants were tested for consistency by applying the usual isotopic relationship [19], $\rho^2 = B'_e/B_e$ with $\rho = [\mu/\mu']^{1/2}$. The lower and upper state rotational constants applied in this relation provide $\rho = 0.97752$ and 0.97726 , respectively, in agreement with the expected value of $\rho = 0.97710$. Analysis of the rotational structure of both isotopomers provides the Ta^{35}Cl – Ta^{37}Cl isotope shift of 2.0262 cm^{-1} . The unusually large magnitude of this isotope shift, especially for a 0–0 band, is probably result of the interaction of the excited state with a close-lying state.

6. Conclusion

The spectrum of TaCl has been investigated in the 3000 – 35000 cm^{-1} region using a Fourier transform spectrometer at the National Solar Observatory at the Kitt Peak and a laser ablation/molecular beam apparatus at the University of New Brunswick. A number of TaCl bands observed over the entire region have been classified into three groups with different lower states, $\Omega'' = 0^+$, 2, and 3. Rotational analysis of a number of bands in the three groups has been carried out and spectroscopic constants have been extracted. To determine the identity of the ground state, two bands, 15684 cm^{-1} band (group I) with $\Omega'' = 0^+$ and 17990 cm^{-1} (group II) with $\Omega'' = 2$ were chosen for study as a function of the backing pressure used in the laser ablation/molecular beam experiments. Both of these bands maintained the same relative intensity making it difficult to identify the lowest state. This experiment suggested that the $\Omega'' = 0^+$ and 2 states are very close and very low-lying in energy.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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