

## THE BAND SPECTRA OF THALLIUM IODIDE AND FLUORIDE

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### Plates II A-B

**ABSTRACT.** The band spectra of TII and TIF are reinvestigated in emission in a high frequency discharge under higher dispersion than that employed previously. The analysis of the main system of TII proposed by P. T. Rao and K. R. Rao, has been confirmed. Using the more accurate data obtained in the present work, the following constants have been deduced.

$$\begin{aligned} \nu_0 &= 26362.4 & \omega_1' &= 93.7 & x_1' \omega_1' &= 0.107 \\ \omega_2'' &= 123.2 & x_2'' \omega_2'' &= 0.088 \end{aligned}$$

In each one of these halides a new system has been detected. A vibrational analysis has also been proposed for each, which shows that the lower state is the ground state of the molecule.

The present work is a continuation of a series of investigations carried out by P. T. Rao and K. R. Rao (1949) and P. T. Rao (1950) on the halides of thallium. The characteristic band systems so far observed in each of these halides are briefly summarized in Table I.

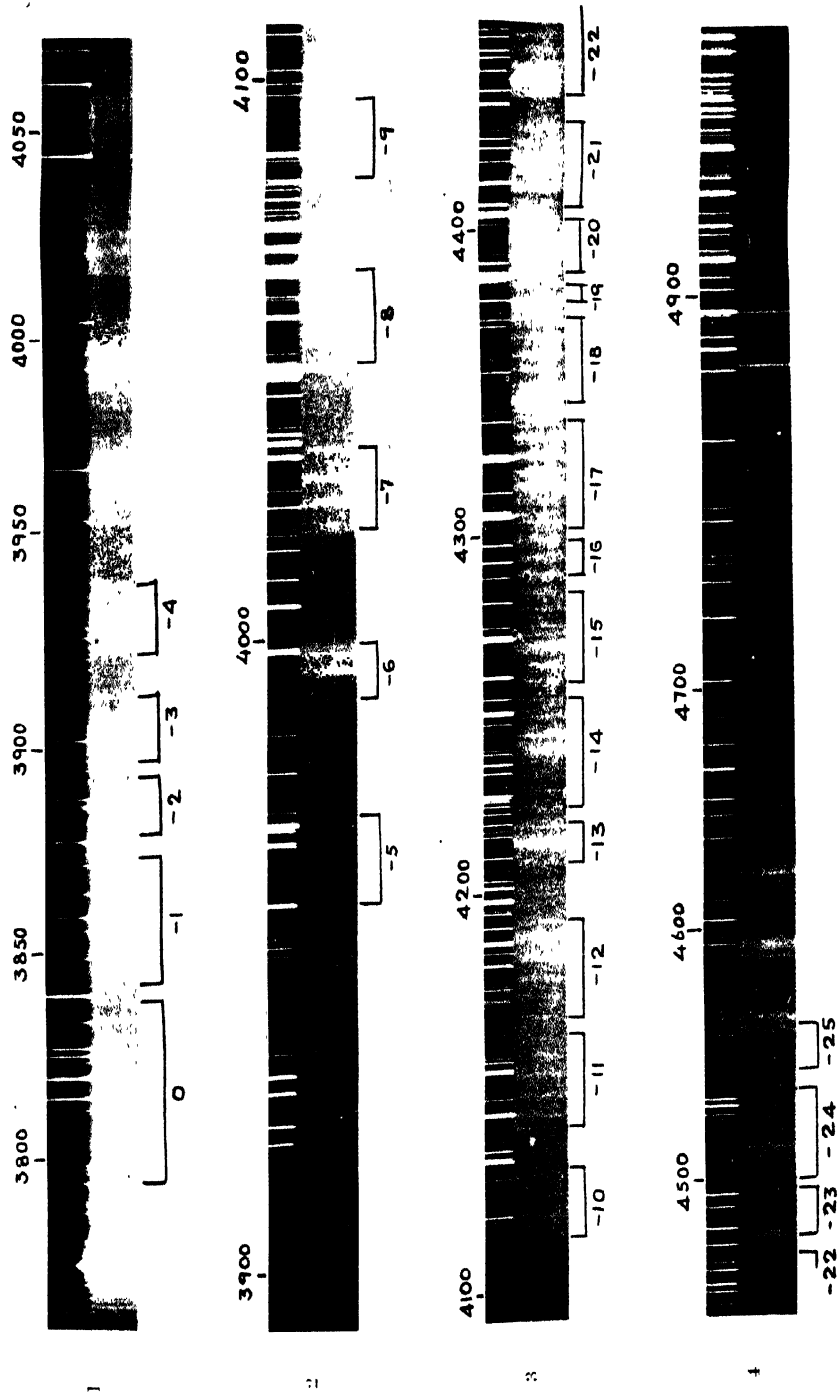
### EXPERIMENTAL

#### *Recording of the spectrum of TII.*

The experimental technique is the same as that employed by Rao and Rao (1949) in the previous investigation. But the low power oscillator (5 watts) used by them to excite the spectrum is replaced by a high power oscillator (100 watts) in the present work. A marked improvement in the structural appearance of the bands is noticed when this source is used. The spectrum is photographed on the following instruments: (1) 10ft. concave grating spectrograph—first order. (2) Three prism glass Littrow spectrograph, and (3) Fuess spectrograph. Exposures for about three to four hours on the grating spectrograph, half an hour on the glass Littrow spectrograph and about fifteen minutes on the Fuess spectrograph gave good pictures. The photographs taken on the above instruments are shown in Plates IIA and IIB.

#### *Description of the Spectrum.*

Plate IIB, figure 5 gives the general appearance of the spectrum from  $\lambda 6300$  to  $\lambda 3800$ . The fall in the general intensity above  $\lambda 4500$  and the increase in the intensity of the bands above  $\lambda 5500$  clearly suggests the occurrence of a new system above  $\lambda 5500$  which will be described later.



III bands  $\Sigma \rightarrow \Sigma$   
 Fig. 1—Grating spectrogram. Figs. 2, 3, 4—Glass Littrow spectrograms

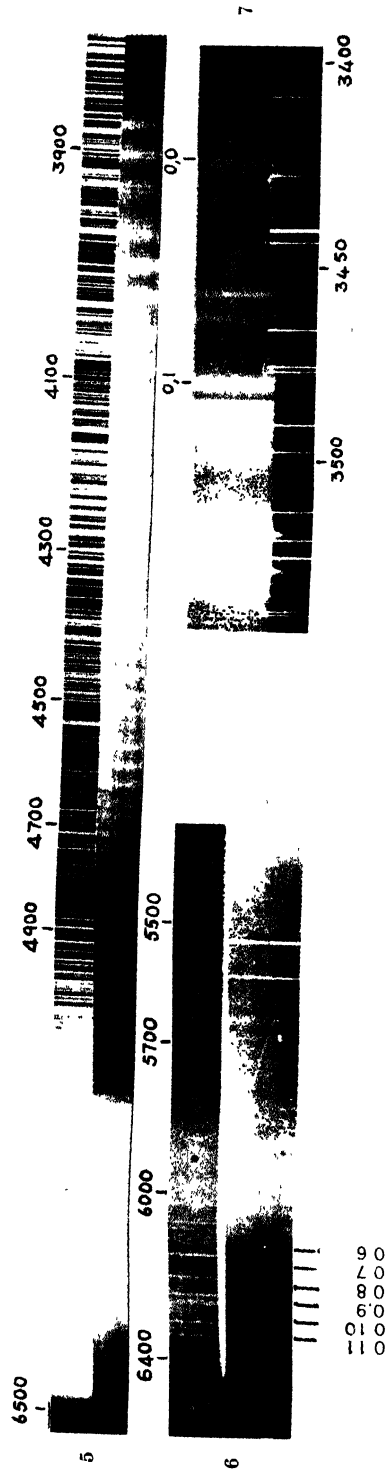


Fig. 5—Thallium iodide bands, system  $\Sigma$  —  $\Sigma$  — Fuess spectrograph overall picture.  
 Fig. 6—TlII bands (6338 Å — 5577 Å) — Fuess spectrogram.  
 Fig. 7—TlI bands (3500 Å — 3400 Å) — Quartz Littrow spectrogram.

TABLE I

Molecule	Author	Region	Transition
TlF	Butkew and Boizowa	$\lambda_{2200}$ (Absorption continuum)	
	Howell and Coulson	$\lambda_{2350} - \lambda_{2200}$	$1\pi \rightarrow 1\Sigma^+$
	"	$\lambda_{2800} - \lambda_{2600}$	$3(\pi)^+ \rightarrow 1\Sigma^+$
	"	$\lambda_{3100} - \lambda_{2800}$	$3I \rightarrow 1\Sigma^+$
TlCl	Butkow, Howell and Coulson	$\lambda_{3400} - \lambda_{3200}$	$3I \rightarrow 1\Sigma^+$
	"	$\lambda_{2545} - \lambda_{2475}$ (Absorption continuum)	
	"	$\lambda_{3105}$ (Absorption continuum)	
	Howell and Coulson	$\lambda_{2890}$ (Absorption continuum)	
	P. T. Rao	$\lambda_{4150} - \lambda_{3800}$	
TlBr	"	$\lambda_{4300} - \lambda_{4150}$	
	Butkow, Howell and Coulson	$\lambda_{4500} - \lambda_{0500}$	$3I \rightarrow 1\Sigma^+$
	"	$\lambda_{5330}$ (Absorption continuum)	
	Howell and Coulson and P. T. R.	$\lambda_{4000} - \lambda_{3950}$	
TII	"	$\lambda_{4050} - \lambda_{3800}$	
	P. T. R. and K. R. R.	$\lambda_{5300} - \lambda_{3800}$	$3I \rightarrow 1\Sigma^+$
	"	$\lambda_{3700} - \lambda_{3600}$	$3\Pi_0^+ \rightarrow 1\Sigma^+$

Plate IIA, figure 1 is a grating spectrogram and figures 2, 3 and 4 are reproductions of photographs taken on the three prism glass Littrow instrument.

The main system attributed to the transition  $3I - 1\Sigma^+$  extends from  $\lambda_{3800} - \lambda_{5300}$  consisting of about 200 bands. Further description of the spectrum is not necessary here as it is well described in Rao and Rao's paper (1949).

A brief system occurring in the region  $\lambda_{5500} - \lambda_{6300}$  shown in Plate IIB, figure 6, consisting of about 25 bands is also ascribed to the thallium iodide molecule.

*Vibrational Constants.*

From a study of the absorption spectrum of the molecule, Rao and Rao

were able to locate the  $\Delta v=0$  sequence between  $\lambda 3795.4$  and  $\lambda 3838.6$ . This necessitated a change in  $v'$ ,  $v''$  numbering of the bands which is adopted here.

The source of error involved in the determination of the vibrational constants arises from the absence of long progressions or sequences and the very low value of the anharmonicity constants. Most of the  $\Delta G(v)$  values are obtained as differences from few band heads. The measurement of the individual band heads should, therefore, be very accurate in the determination of the vibrational constants. As such, a number of plates are taken on the grating spectrograph and for measurements in the region  $\lambda 3800$  to  $\lambda 4000$  these plates are used. Above  $\lambda 4000$  the bands are found unsuitable for measurement on the plates taken on the grating and, therefore, plates taken on the three-prism glass Littrow spectrograph are measured. Band head data upto  $\lambda 4500$  are only used in the calculation of the vibrational constants as the bands upto this limit can be accurately measured.

Adopting the same scheme of classification (Rao and Rao, 1949) a graphical method has been employed to estimate the constants for the upper and the lower states. The estimated constants are

$$\begin{aligned} \omega_r' &= 93.7 & x_r' \omega_r' &= 0.107 \\ v_r &= 26362.4 \\ \omega_r'' &= 123.2 & x_r'' \omega_r'' &= 0.088 \end{aligned}$$

The system origin is calculated from the measurements of several bands in the entire range. There is a close agreement between the observed and calculated values of the wave numbers.

#### Determination of $D'$ of TII.

The ground state of TII may be assumed to arise from a combination of two neutral atoms ( $Tl^2P + I^2P$ ) and the upper state from a combination of ( $ex Tl^2S + unex I^2P$ ). If this assumption is correct the energy of dissociation of the ground state ( $J''$ ) can be deduced indirectly as follows. The value of  $D'$  is determined by Birge and Spomer's method. Using this value of  $D'$ ,  $D''$  is obtained from the following formula

$$v_r + J' = J'' + v_{atom}.$$

The value of  $v_{atom}$  is the difference between the ground term  $^2P_{1/2} = 49264.2$  and the first excited state  $^2S = 22786.7$  of Tl, I.

$$\begin{aligned} v_{atom} &= 26477.5 \text{ cm}^{-1} \\ D' &= 20513.8 \end{aligned}$$

From the values of  $v_r$ ,  $D'$  and  $v_{atom}$ ,  $D''$  is obtained as equal to  $20398.2 \text{ cm}^{-1}$  and in electron-volts it is equal to 2.53. This value is found to be in good agreement with the thermochemical and atomic fluorescence data.

#### DISCUSSION OF THE ANALYSIS

The main difficulty experienced by Rao and Rao in the vibrational analysis of the main system of TII is in respect of the magnitude of the

values of  $\omega_e'$  and  $\omega_e''$ . Several alternatives of choice are available. The interval of about  $30 \text{ cm}^{-1}$  between the equispaced components in each sequence suggests the approximate value of the difference between  $\omega_e'$  and  $\omega_e''$ . The individual values may be any one of the following sets.

$\omega_e'$	$\omega_e''$
90	120
120	150
150	180
180	210

Of these Rao and Rao preferred the set 90 and 120 from a comparison of the ground state constants of the halides of mercury, thallium, lead and bismuth and also from a comparison of the vibrational constants of thallium halides. Petrikaln and Hochberg (1933) have quoted a value 150 for  $\omega_e''$ . The agreement between the deduced value of the energy of dissociation and its value derived from other methods (thermochemical and atomic fluorescence methods) shows that the set of constants 90 and 120 is the most probable one. However, the value of  $D''$  deduced directly from Birge and Sponer's method using the value of 123.2 for  $\omega_e''$  is somewhat high. In case a value for  $\omega_e''$  of the order of 150 is adopted,  $D''$  would be still higher and deviate far from the true value. It is, therefore, believed that 120 is the right order of magnitude for  $\omega_e''$ .

*New Observations in the Band Spectrum of Thallium Iodide.*

As shown in Plate IIB, figure 5 the increase in the general intensity of the spectrum above  $\lambda 5500$  suggests that the bands in the region  $\lambda 5550 - \lambda 6340$  might belong to a new system arising in a new electronic transition. In obtaining these bands great care has been taken to suppress the emission bands of iodine which occur in the same region. These iodine bands are recorded on some of the plates when there is a slight leak in the vacuum system. Further optimum conditions of heating the discharge tube are found necessary for a good reproduction of the bands. These bands are shown in Plate IIB, figure 6.

There are about 25 bands, most of which are broad and diffuse, their direction of degradation being uncertain. A tentative vibrational scheme has been proposed for these bands as shown in Table II. A clue for the analysis has been afforded by the ground state progression with  $v'=0$ . The lower state of this system appears to be common to that of the main system. The approximate values for the vibrational constants are as follows.

$$\begin{aligned} \omega_e' &\sim 79 \\ \omega_e'' &\sim 126 \end{aligned}$$

TABLE II

$\nu''$	0	1	2	3	4	5	6	7	8	9	10	11	$\Delta G(\nu'')$
0					16625 S 76.3	16511	16376.3	16252.8	16134.0	16010.2	15891.6	15772.0	
1	17070.7 75.8		16839.8		16702.1								76.3
2	17279.5 80.7	17156.5											76.8
3	17360.2 72.1												80.7
4	17432.3 67.1												72.1
5	17499.4 74.8												67.1
6	17574.2												74.8
$\Delta G(\nu'')$	133.0		127.7		124.1	125.4	123.5	118.8	123.8	118.6	119.6		

The wavelength and other data of the bands are shown in Table III.  
*The Band spectrum of Thallium fluoride.*

The band spectrum of thallium fluoride was extensively studied both in emission and in absorption by Howell (1937) as a part of a series of investigations on the molecular spectra of heavy diatomic fluorides HgF, TlF, PbF and BiF. The band systems reported and analysed by him are briefly summarized in Table IV.

TABLE III

Wavelength	Int.	Wavenumber	Classification
6338.6	2	15772.0	0,11
6306.7	2	15851.8	
6290.9	2	15891.6	0,10
6244.3	2	16010.2	0,9
6196.4	2	16134.0	0,8
6151.1	2	16252.8	0,7
6134.1	2	16297.8	
6104.7	2	16376.3	0,6
6069.7	2	16470.7	
6158.3	3	16511.7	0,5
6013.1	5	16625.8	0,4
5985.6	5	16702.1	1,4
5962.0	5	16768.3	
5940.2	5	16829.8	1,3
5922.3	5	16880.7	
5871.8	3	17025.8	
5853.3	3	17079.7	1,1
5827.1	3	17156.5	2,1
5785.6	3	17279.5	2,0
5758.7	2	17360.2	3,0
5734.9	3	17432.3	4,0
5712.9	3	17499.4	5,0
5688.6	3	17574.2	6,0
5663.7	4	17651.4	
5577.0	2	17925.8	

TABLE IV

Level	$\nu_e$	$\omega_e$	$x_e \omega_e$
$^1\Pi$	45500.	360	—
$^3(\Sigma)_+$	36869.5	360.65	12.25
$^3\Pi$	35180.7	439.87	8.60
$^1\Sigma$	0	475.00	1.89

No band systems corresponding to those observed in TlCl and TlBr by P. T. Rao (1950), Howell and Coulson, or to those reported for TlI in the present work are so far reported for this molecule. As a continuation of the work on TlI bands the authors photographed the spectrum of TlF in



the visible and near ultraviolet regions, under the same experimental conditions of excitation employed for photographing the TII spectrum.

Characteristic bands attributable to TIF were recorded in the region  $\lambda_{3400}-\lambda_{3500}$ , some of which have a similar appearance to those observed by Howell in the region  $\lambda_{2800}-\lambda_{3200}$  analysed into two systems. These bands were also recorded on our plates. Plate IIB, figure 7 is a reproduction of the brief system obtained in the present investigation. There are about 7 bands. A peculiarity of the appearance of the bands observed by Howell is the occurrence of the so called "absorption lines" in the emission spectrum which were interpreted by him as the gaps produced by the missing lines around the band origins. The same peculiarity is noticed in the 0,0 and 0,1 bands of the present system for which a brief vibrational array is shown in Table V. The lower state of the system appears to be the ground state and the same as the lower state of the two ultraviolet systems. This system is then analogous to the new system reported for TII in the present work.

TABLE V

$v'$	$v''$	0		1		2	$\Delta G(v')$
0		29208.4	477.3	28731.1 191.3	470.4		191.3
1				28622.4		28452.0 185.2	185.2
2			477.3		470.4	28637.2	
	$\Delta G(v'')$						

The following are the approximate values for  $\omega_e'$  and  $\omega_e''$

$$\omega_e' \sim 194$$

$$\omega_e'' \sim 481$$

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