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THE COMPLEX BAND SPECTRUM OF TITANIUM CHLORIDE
(THE DIATOMIC MOLECULE, TiCl)

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Plate XXVII

ABSTRACT. The characteristic band spectrum of the titanium chloride molecule has been obatined more extensively than that recorded by More and Parker in a transformer discharge through the vapour. The bands are divided into two systems:

$$\text{System I: from } \lambda 4206 - 4031$$

$$\text{System II: } ,, \quad \lambda 4072 - 3787.$$

The systems are analysed on the assumption of the respective electronic transitions

$$^4\Pi - {}^4\Sigma \text{ and } \Sigma^1 - {}^4\Sigma$$

The approximate vibrational constants are:

	ν_r	ω_r'	$x_r'\omega_r'$	ω_r''	$r_r''\omega_r''$
System II	25000	474	4.4	455	3.8
System I	23810	531	1.5	455	3.8

INTRODUCTION

The prominent band at λ 4192 is known for a long time and was first reported by Fowler (1907) along with two others at λ 4199 and λ 4188, and ascribed to the molecule TiCl. More and Parker (1937) recorded about 32 bands of this molecule in the region λ 4200—4000. They presented a fragmentary analysis of this group of bands assigning five bands to each of the 0,0 ; 1,1 etc., vibrational members. The heads are mentioned as forming either P_1 or P_2. Approximate vibrational constants are also suggested by them as $\omega_e' = 498.3$ and $\omega_e'' = 4.13$. Besides the violet of the above group of bands other groups were mentioned as occurring in fragmentary groups. For these even the wave-length data are not reported. Following the author's work on the complex band spectra chiefly of the halides of chromium, it is considered useful to study the band spectra of the halides of titanium which belongs to the same horizontal row as chromium. Vanadium occurs between Ti and Cr but the preparation of the halides has presented to us very serious difficulties, nor could these halides be supplied by Johnson and Mathey. A specimen of the chloride of Ti was available in a high degree of purity (supplied by Merck) and the band spectrum of this has been investigated. The results are described in this paper.

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E X P E R I M E N T A L

More and Parker excited the bands in low and high frequency discharges through flowing vapour of TiCl₄. They found the high frequency discharge more intense than the low frequency one. In our work, the pure Merck product of TiCl₄ is introduced into the usual H-shaped discharge tube and a low frequency discharge from an ordinary 1/4 K.W. transformer is passed through the vapour. TiCl₄, being a liquid at room temperature (about 30°C), is placed in a container and is supplied in a regular stream controlled by a stopper from one end of the tube, while the tube is evacuated from the other end. As the vapour is corrosive a series of effective absorption towers are placed between the pump and discharge tube, partially to protect pump from the effect of chlorine or HCl A characteristic bluish white discharge is obtained at a particular pressure which is maintained steadily by adjusting the stop-cock from time to time Photographs are taken on the quartz Littrow spectrograph on Ilford special rapid plates. Exposures of 2 to 5 hours were given on account of the low intensity of the bands : good plates are obtained with 5 hours exposure. (Plate XXVII.)

D E S C R I P T I O N O F T H E S P E C T R U M

The bands obtained by the author are in six groups and reproduced in Plate XXVII. The intensity distribution in each group is not as regular as might be expected in a simple structure. The bands are line-like as in the other complex halides. Of these six groups the one at λ 4192, as can be seen from the reproduction, is conspicuously intense and is the band that was first reported by Fowler. Another marked feature of this is that it is developed unusually long and definitely impresses as a long sequence structure. As mentioned by the previous authors it corresponds to the $\Delta v = o$ group. Its intensity makes the identification unmistakable.

The other five groups occur to the violet of this prominent group and are of much less intensity. But there are no groups or bands towards the long-wavelength side of λ 4192. This feature is conspicuously different from the spectra of the chlorides of chromium and manganese in which there is a development of the groups on either side of the prominent one corresponding to $\Delta v = o$. However, in general, an examination of the complex spectra has shown that the (1,0) group is of considerable intensity and even comparable with the (0,0) group while the (0,1) group is much less intense. This might account for the absence of the groups on the red side of λ 4192 of TiCl. The (0,1) group is far too weak to be recorded.

All the six groups mentioned above could not be considered as belonging to one system. As we proceed from λ 4192 towards shorter wave-lengths we find the group at λ 3857 (the fourth group) shows a sudden rise in

PLATE XXV

RAO
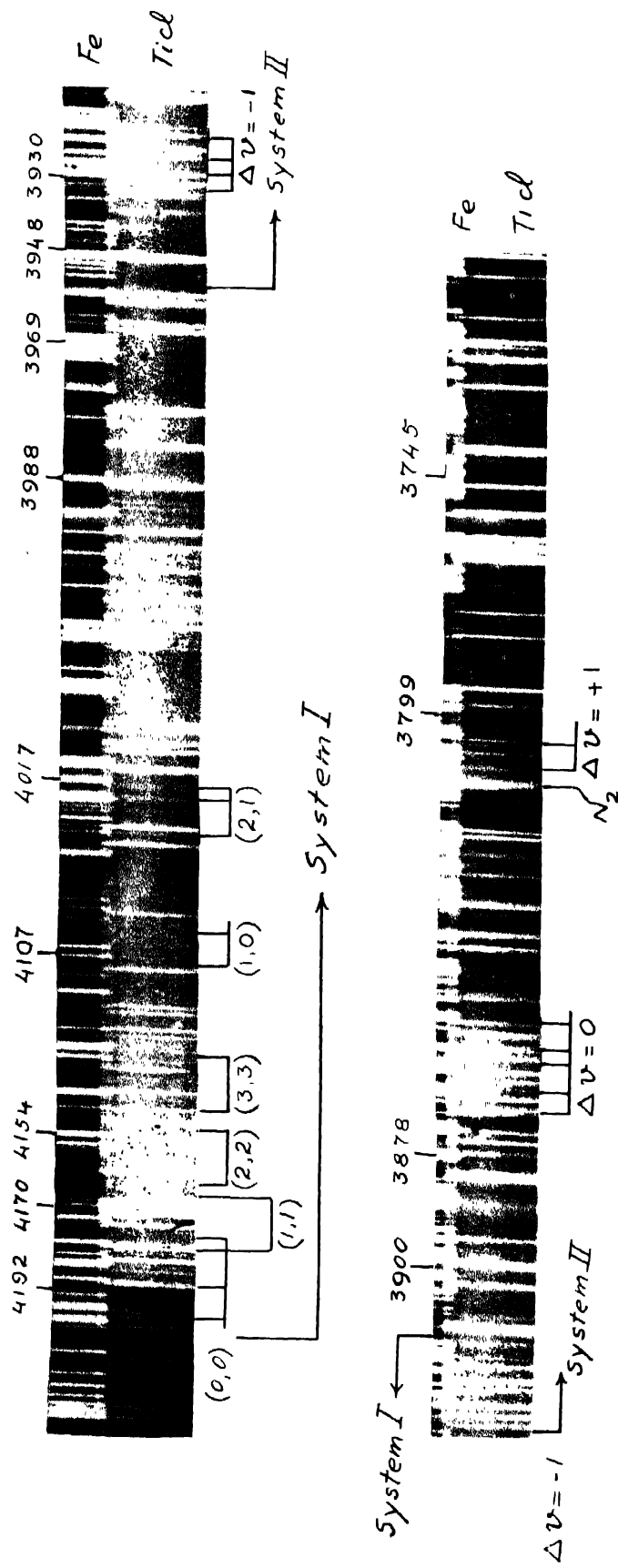
Titanium chloride bands.

intensity. This had to be regarded as the $\Delta v = 0$ group of another system. A similar feature is observed in the band groups of FeCl considered by Muller (1943) : a rise in intensity at a particular group being interpreted as a starting point of another system.

The characteristic bands of TiCl are hence divided into two different systems : λ 4192 being the (o,o) of system I and λ 3857, the corresponding number of system II.
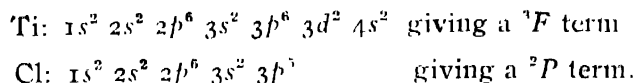
STRUCTURE AND ANALYSIS OF THE BANDS

The structure of λ 4192 belonging to system I is much more complex than that of 3857 assigned to system II In order to interpret the structure of these two systems the following discussion may be helpful. In fact the analysis is suggested as a result of this discussion

Considering the total number of electrons in TiCl molecule, the multiplicity of the terms involved should be even: and as Ti atom has two electrons less than the Cr atom it is reasonable to expect the multiplicity to be four. The following variation of the multiplicities with atom may be instructive:

Molecule	Mn x	Cr x	V x	Ti x	Sc x	Ca x	K x
Multiplicity	7	6	5?	4	3	2	1

(x represents hydrogen or halogen atom.)

The titanium atom with 22 electrons and the chlorine atom with 17 electrons have the following electronic configurations:

Ti: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$ giving a ^3F term

Cl: $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ giving a ^2P term.

The incomplete $3d^2$ and $3p^5$ groups give rise to the respective atomic terms. In the process of formation of the molecule, the following electron configuration may be imagined :

$$\sigma^2\pi^3,\ \sigma\pi^2 \qquad ^4\Sigma$$
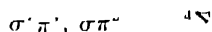
With the spins all parallel, the total spin is 3/2 giving a multiplicity 4. When the spins are parallel the m_l values of the π electrons are of opposite sign according to Pauli's exclusion principle, and $\Sigma m_l = 0$, resulting in a Σ state. An upper state may arise from $\sigma^2\pi^4$, π^2, $\pi \rightarrow ^4\Pi$ by the elevation of the σ electron to a Π level.

It is easy now to formulate the possible rotational heads for the transition $^4\Pi - ^4\Sigma$. The ground state $^4\Sigma$ must correspond to the coupling type, Hund's case (b). In a Σ state, ($\lambda = 0$), there is a spin splitting of each rotational level, i.e. for each value of K there will be component levels, with J lying between $(K-S)$ and $(K+S)$ which, following Mulliken, may be designated as (F_4, F_3, F_2, F_1) respectively. These levels have very small separations and ordinarily are not resolvable. The upper $^4\Pi$ state may

approximate to case (a) or case (b) or may represent any state intermediate between the two. In fact, in analogy with the CrCl transition, we have here the four levels F_4, F_3, F_2, F_1 corresponding to $\lambda + 1\frac{1}{2}$ to $\lambda - 1\frac{1}{2}$ (the Ω values).

A schematic diagram for the transitions $^4\Pi - {}^1\Sigma$ representing the various observable branches is given in Fig. 1. The form of the branches is indicated exactly as in the sextet transition of CrCl. For the rotational formula,
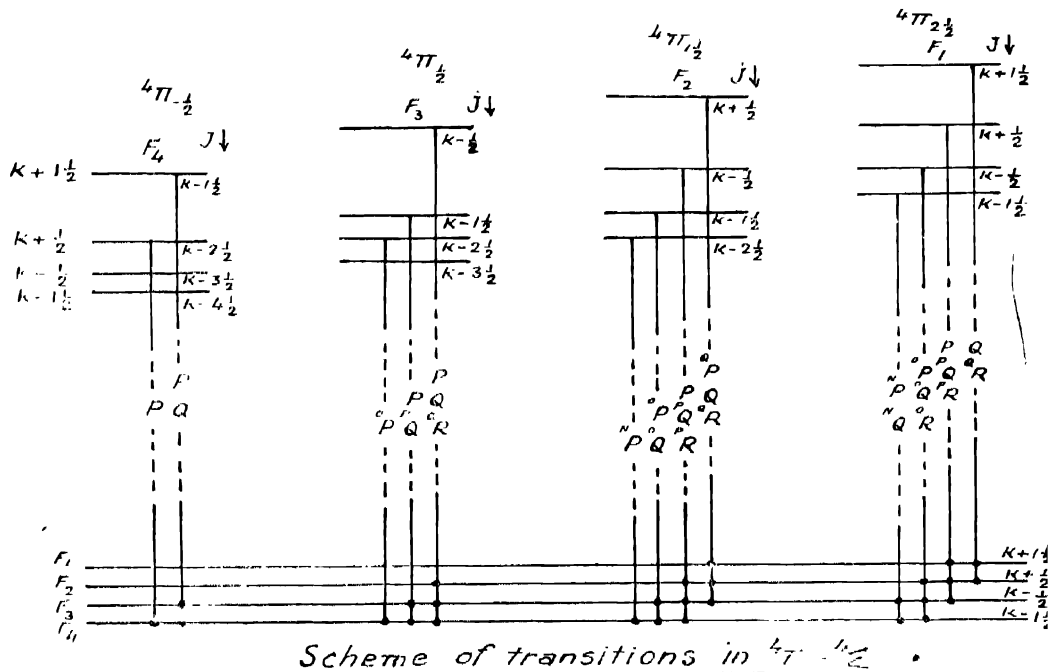

FIG. 1

etc.—reference may be made to our earlier discussion on the sextet transition (Rao and Rao, 1949).

As the bands of TiCl are conspicuously violet-degraded ($\omega_e' > \omega_e''$) we expect only the Q, P, O, and N forms as head-forming. These transitions only are shown in Fig. 1 and collected in Table 1.

Another upper state can be postulated by imagining an electronic configuration

$$^2\pi^4, \pi^2\delta- \quad \cdot {}^{IV}$$

in which one electron of the previous π^2 group is excited to a δ state. Here too the spins are parallel but while the m_l's are parallel for the π electrons that for the δ electron is anti-parallel, thus resulting in a Σ term again. Transitions between this state and the ground state should be naturally resulting in a simple band structure as both the states are $^1\Sigma$, and the bands should be to the violet side of the previous group. System I is considered as probably due to the transition $^4\Pi - {}^4\Sigma$ and system II as $^1\Sigma - {}^1\Sigma$.

System II :— With the above picture of the expected transitions an analysis of the bands in system II is first attempted. In this process,

the vibrational constants given by More and Parker were helpful for preliminary attempts. (These constants were derived by them from the analysis of the group between $\lambda 4200$ to 4000 *i.e.* of the system I)

TABLE I
List of Theoretical Transitions.

ΔJ	-1	o	$+1$	Symbol.
P_4				A
$^aP_{13}$		O_1		B
$^oP_{34}$				C
P_3		$^rQ_{31}$		D
$^oP_{32}$		Q_3	$^qR_{31}$	E
$^NP_{21}$				F
$^oP_{23}$		Q_{21}		G
P_2		$^rQ_{23}$	$^pR_{24}$	H
$^qP_{21}$		Q_2	$^oR_{2?}$	I
$^NP_{13}$		$^KQ_{11}$		J
$^oP_{12}$		$^oQ_{13}$	$^oR_{11}$	K
P_1		$^rQ_{12}$	$^pR_{13}$	L
		Q_1	$^qR_{12}$	M

The group at $\lambda\ 3867.9$ is taken as a starting point as it is expected to correspond to the $\Delta v = o$ of system II due to the simpler transition $^4\Sigma - ^4\Sigma$. With this start and with the help of the approximate ground state frequency 441, suggested by More and Parker, attempts have been made to detect regularities among these bands. They resulted in the identification of bands with simple sequence structure involving the interval difference of about 437, which is just very slightly different from the ground state frequency derived by More and Parker. The neighbouring groups fitted into a regular and simple sequences developing to large v', v'' values. The upper state has the first difference of 460 cm^{-1} which is of the proper order of magnitude. Most of the bands have entered into this analysis easily and the Deslander's scheme is given in Table II. By treating the system as a separate one, it is possible to explain easily the abnormal intensity of the group at $\lambda\ 3867$ which corresponds to the $\Delta v = o$ sequence. In manganese an analogous system is observed and analysed by Rochester and Olsson (1939) and is explained by Bacher (1948) as due to the $^7\Sigma - ^7\Sigma$ transition. In the case of chromium the corresponding system has not been obtained as yet. As already pointed out earlier (Rao and Rao, 1949) the group at $\lambda 2600$ region, reported by Nesnage has been identified by

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TABLE II

Deslander's Scheme for TiCl System II

	0	(437.1)	1	(435.4)	2	(430.8)	3	(418.8)	4	(414.4)	5	(406.1)	6	(386.8)	7	(379.9)	8
0 (460.1)	25846.4(3)		25409.3(5) 459.5		25432.3(0) (459.6)		24546.4(3)										
1 (458.5)	26307.2(3) (438.4)		25868.8(5) (457.3)														
2 (442)			26326.1(b)		25891.9(5 b) (44.6)		25465.2(0, ?)		25039.5(0) (443.4)		25027.4(1) (442.0)						
3 (435.8)					26332.5.2		25991.7(2) 437.8		25582.9(0) (433.7)		25069.4 1		24663.5(1)				
4 (435)							26337.5(b)		25916.6(5 (435.2)								
5 (430)									26351.8 (417.8)		25934.3(1) (430.2)		25525.1(1) 429.5				
6 (418)											26364.5		25957.6(3) (418.1)		25570.2(0) (419.3)		
7													26375.7(3)	(387.4)	25989.5(5 b) (386.2)		
8															24700.1(9)		24755.4(1)

Gaydon (1927) as due to AlCl. Attempts by the author to obtain the group in CrCl have been inconclusive though it must be mentioned that there is a definite indication of the existence of the bands in the above region and quite distinct from the AlCl bands. However, the analysis of the bands of TiCl on the basis that they constitute two systems, is believed to be correct, and it is expected to be of a similar transition as the corresponding bands in other molecules.

Analysis of System I:—In the light of the postulates given earlier the 13 band heads belonging to the particular (v',v'') values align themselves thus (Table III).

TABLE III

v''

		F_1	F_4	F_2	F_1
	Q	B	B	I	M
v'	P	A	D	H	L
	O		C	G	K
	H			F	J

Having obtained the ground state difference for system II attempts are now made to build up the analysis of the first system. Values of ground state differences obtained by us are used for the identification of the sequence members. The band at λ 4192 is unmistakably the (o,o) band. In the (o,o) group regularities of the band heads of the order of about 30 cm^{-1} are observed. A comparison of the multiplet separations in CrCl and MnCl etc., gave 30 units as the approximate order of multiplet separations to be expected in the case of TiCl. Further, a study of the ^4P term in scandium I and Ti II and ^5P in Ti I, also gave a separation factor of the order of 30 cm^{-1}. This led us to attempt to secure regularities with about 30 as the multiplet separations, and so in each group are placed four members with that separation. These included most of the bands assigned by More and Parker to the (o,o) group. On building up the analysis we observed that the first vibrational difference in the upper state we obtained, was about 530 cm^{-1} whereas that due to More and Parker was 498 cm^{-1}; differing by 32 cm^{-1}. This is our multiplet separation, indeed. Evidently the previous authors did not chose the corresponding components in deriving the correct intervals. On a proper choice we arrive at the ground state difference 444, which also agrees very well with their values. This coincidence is taken as an additional support for our analysis. It is further gratifying to see that most of the bands assigned by More and Parker as belonging to a particular group (notably the o,o and 1,1 groups) go again into the same groups though the analysis is made from

a totally different view-point. Discrepancies are, however, noted and given in the catalogue of the wave-lengths with the assignments of the bands, in Table V. They might be attributed to the fact that our values differ from their values, and also we assign about 13 bands to each (v', v'') value. While the multiplet separations are found to be of the order of 30, the differences of the rotational heads are found to be of the order 7 to 12. The tendency for the separations to increase from F_1 to F_j and also from Q to N branches is also brought out in Table IV.

The very considerable length of the (o, o) group is a characteristic feature in the analysis ; it is a sequence developing up to high (v', v'') values. This feature is not present in CrCl and MnCl bands. This may explain why we do not get the other sequences so well developed in TiCl. Perhaps the entire intensity of the spectrum is thrown into the $\Delta v = o$ sequence, as is also the case in system II, as can be seen from the picture. The (1,o) band of More and Parker is again one of the (1,o) group in our analysis. Two bands at v 24069.4 and v 24136.3 assigned by the previous authors do not find a place in our scheme ; the latter was not even observed on our plates.

In Table V a catalogue of the wave-lengths together with the intensities and wave-numbers are given. Column 5 gives the vibrational assignment. The rotational designation of each head, denoted arbitrarily for convenience by symbols A, B, C, etc., is given in the sixth column. The meaning of the arbitrary symbols A to H, is that, the corresponding actual heads which they represent will be clear from the Table I. The wave-numbers and intensities given in columns 7 and 8 are due to More and Parker and their assignment is also given for the purpose of comparison and clearness.

The scheme shows that practically all the bands have been interperted on the assumptions made; and the manner in which almost all the bands fit in, is taken as evidence in favour of our analysis. This interpretation places TiCl on a par with the corresponding halides in the horizontal row of the first transition group of elements, and brings out not merely the well-known law of alternating multiplicities but also one of progressive increase in multiplicities from group I to group VI elements.

As can be seen from the picture and analysis, one helpful factor in the complexity of the structure is that there is not much overlapping between members of the same sequence. The spread of the multiplet is 120 cms^{-1}, much smaller than the vibrational differences so that there is no overlap of members of different sequences.

The separation between the two systems is much smaller than what is observed in (Cr and) Mn halides.

More and Parker attributed three bands as due to an isotope of chlorine. A search for isotope effect in complex spectra of this type is not considered practicable, particularly under the dispersion we are able

TABLE V

Author			Symbol	More and Parker		
Wave number	Int.	$v'\ v''$		Wave number	Int.	$v'\ v''$
23763.8	0					
23807.9	1	0,0	A	23805.6	1	0,0
23816.2	1	0,0	B			
23820.5	1			23844.5	10	0,0
23845.0	10		E			
23850.6	1	0,0	F			
23857.4	2	0,0	G			
23866.7	5	0,0	H	23864.8	4	0,0
23874.7	4	0,0	I	23871.3	8	0,0
23892.1	4	0,0	K	23890.8	6	0,0
23899.7	6	1,1	A	23899.1	0	1,1
23907.6	2	0,0 1,1	M B	23906.4	5	0,0
23920.6	1	1,1	C	23920.5	4	1,1
23933.3	6	1,1	D	23930.8	8	1,1
23938.3	8	1,1	E	23946.3	5	1,1
23952.5	7	1,1	G			
23959.2	7	1,1	H	23961.3	0	2,2
23968.9	5	1,1	I	23965.1	3	1,1
23977.4	1	1,1	I			
23982.5	1	1,1	K	23983.4	4	2,2
23990.1	1	1,1	L			
23996.0	3	2,2	A	23995.6	7	2,2
24000.8	4	1,1	M			
24008.1	1	2,2	B			
24016.4	1	2,2	C	24013.5	5	2,2
24022.3	4					
24026.5	4	2,2	D	24030.1	0	3,3
24034.0	5	2,2	E	24033.7	61	2,2
24041.3	5	2,2	F			
24051.4	3	2,2	G			
24056.7	3	2,2	H	24057.4	61	3,3

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TABLE V (contd.)

Author			Symbol	More and Parker		
Wave number	Int.	v' v"		Wave number	Int	v' v"
24063.6	3	2,2	l			
24069.4	3			24069.5	5	3,3
24075.1	2	2,2	J			
24084.4	8bl	2,2	K			
24090.1	3	2,2	L	24090.0	bl	3,3
24096.6	1	2,2	M			
		3,3	A			
24103.6	3	3,3	B	24106.8		4,4
24117.8	2					
24123.3	1	3,3	C			
24129.7	3	3,3	D			
				24136.3	3	4,4
24148.0	2	3,3	F	24147.4	2	4,4
24163.5	5bl	3,3	H			
24175.6	0	3,3	I	24178.3	1	4,4
24190.2	3bl	3,3	L	24191.7	bl	5,5
24198.7	3bl	3,3	M			
24209.5	5bl	4,4	A	24206.3		4,4
24219.4	5bl	4,4	B			
				24225.2	0	5,5
24230.7	1	4,4	C	24233.1	0	5,5
24242.8	6bl	4,4	D			
24251.9	3bl	4,4	E			
24262.9	1	4,4	G			
24284.0	0	4,4	J	24274.6	0	5,5
24320.0	0					
24326.6	1					
24341.8	1	1,0	A	24342.8	3	1,0
24352.4	1	1,0	B			
24358.3	1	1,0	C			
				24392.3	2	2,1

TABLE V (*contd.*)

List of unclassified bands

Wave number	Inten	Wave number	Intens
24474.6	1	25452.6	0
24769.6	2	25582.5	1
24884.7	1	25650.0	1
25046.5	1	25858.9	2
25082.8	2	25880.3	4bl
25294.0	0	25924.4	3
25307.1	1	26295.8	1
25340 7	2	26318.5	1
25358.9	2	26358.3	1
25385.4	4	26401 5	0
25417.8	1		

to use. The order of isotope shifts is the same as the order of separation of rotational heads and unless very accurate data are available, preferably quantitative microphotometric measurement of intensities and wave-lengths on spectra obtained under high dispersion, we cannot be very certain about the isotope effect.

The following approximate vibrational constants as obtained in the present investigation are collected in Table VI :

TABLE VI

	ν_e	ω_e'	$x_e'\,\omega_e'$	ω_e''	$x_e''\,\omega_e''$	Λ
System II	25900	474	4.4	455	3.8	—
System I	23810	534	1.5	455	3.8	30

R E F E R E N C E S

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