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THE EMISSION SPECTRUM OF VO MOLECULE

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(Plate 3)

ABSTRACT. The emission spectrum of VO in the visible region has been reinvestigated. Twentynine new bands observed for the first time have been reported. Some of these have been fitted into the scheme proposed by Mahanti (1935) extending the scheme to higher quantum numbers. The vibrational constants estimated from the analysis of the authors' data are found to give better agreement with the observed values than those obtained by earlier workers. It has been shown that some of the unidentified bands observed by Fergusson (1932) can be accommodated in the infra-red system reported by Keenan and Schroeder (1952).

The spectrum of VO in the visible region was investigated by Fergusson (1932) and later more extensively by Mahanti (1935) and by Lagerqvist and Selin (1957b). Keenan and Schroeder (1952) have obtained a further system in the region $\lambda 6477\text{Å}—\lambda 8666\text{Å}$. Still further, in the infra-red, in the region $\lambda 9530\text{Å}—\lambda 10462\text{Å}$, some more bands have been observed by Lagerqvist and Selin (1957a).

The rotational analyses of certain bands of this molecule made by Mahanti (1935) were found by Lagerqvist and Selin (1957b) to be faulty. The constants obtained from a fresh analysis carried out by them differed from those of Mahanti.

We present in this paper our observations on the spectrum of VO which, we hope, will be of interest, in the light of findings of earlier workers.

EXPERIMENTAL

A D.C. arc run at 250 volts in air at atmospheric pressure was used for the excitation of the molecule. The lower electrode was fed with vanadium pentoxide powder and the arc was run at the constant current of 1 amp. All precautions were taken to reduce the A.C. ripple to minimum, which was otherwise menacingly strong.

The spectra were taken on a Steinheil 3 prism glass spectrograph with two different lens combinations and also on a Cenco 1 metre grating spectrograph.

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RESULTS, OBSERVATIONS AND DISCUSSION

As stated above, spectra were taken with instruments having different dispersions. Measurements were made under all these dispersions on what appeared to be the vibrational band-heads. Of a large number of such measurements made, only those corresponding to the heads that appeared to be convincing are reported here.

The spectrum which we have obtained is, in totality, more complex than that reported by Fergusson (1932) and Mahanti (1935). In fact, the close groupings of six or seven bands observed at recurring intervals and the appearance of line like bands led us to believe that the spectrum obtained in our investigation is similar to that obtained by Keenan and Schroeder (1952) in the infra-red. Incidentally, Keenan and Schroeder had also used V_2O_5 powder for the excitation of the molecule and we felt it worthwhile to follow his procedure of vibrational analysis, in which he had assumed eight components for a single vibrational transition. But our efforts in that direction proved futile. Rotational structure was open to different degrees on plates of both low and high dispersion. This feature is rather unfortunate for a vibrational analysis, a definite location of the band-head being not always easy. There were also some spurious band-heads which are deceptive, and sufficient care has been taken to eliminate these.

Table 1

Band-heads of VO

Wavelengths A°	Wavenumbers			Transition $v'-v''$
	Present Authors	Mahanti	Fergusson	
6588.90	15172.9	15172.9	15174.0	2—4
6531.47	15306.3	15303.2	15306.0	1—3
6477.92	15432.8	15433.1	15433.0	0—2
6418.84	15574.8	15575.7	—	6—7
6398.39	15624.6	—	—	—
6384.00	15659.8	—	—	—
6360.34	15718.0	15717.9	—	5—6
6333.35	15785.0	—	—	—
6329.12	15795.5	—	—	—
—	—	15860.3	—	4—5
6295.16	15880.9	—	—	—
—	—	16002.7	—	3—4
—	—	16146.5	—	2—3
6166.59	16211.9	—	—	8—8*
6138.78	16285.4	16284.5	—	1—2

Table 1 (*Contd.*)

Wavelengths A°	Wavenumbers			Transition v'—v"
	Present Authors	Mahanti	Fergusson	
6107.99	16367.6	—	—	7—7*
6086.49	16425.3	16425.4	16428.0	0—1
6053.26	16515.4	—	—	6—6*
6032.25	16573.0	—	—	—
6021.85	16601.9	—	—	—
6012.72	16626.8	—	—	—
5998.98	16664.8	—	—	—
5996.00	16673.1	16668.7	—	5—5
5986.57	16699.4	—	—	—
5942.47	16823.3	16823.3	—	4—4
5919.37	16888.9	—	—	—
5914.49	16902.8	—	—	—
5910.06	16915.3	—	—	—
5905.23	16929.3	—	—	—
5901.32	16940.5	—	—	—
5888.62	16977.2	—	—	3—3*
5836.51	17128.8	17126.5	17125	2—2
5830.84	17145.4	—	—	8—7*
5786.34	17277.3	17277.1	—	1—1
5776.19	17307.6	—	—	7—6*
5737.29	17425.0	17426.9	17425	0—0
5723.80	17466.1	17466.1	—	6—5
5696.51	17549.8	—	—	—
5669.84	17632.4	17632.1	—	5—4
5617.18	17797.6	17795.0	—	4—3
—	—	17955.8	—	3—2
5527.38	18086.7	—	—	8—6*
5516.67	18121.8	18119.8	18123	2—1
5475.54	18257.1	—	—	7—5*
5469.42	18278.4	18278.8	18279	1—0
5424.77	18428.8	18427.7	—	6—4
5373.46	18604.8	18605.4	—	5—3
5324.60	18777.5	18775.9	18877.9	4—2

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Table 1 (*Contd.*)

Wavelengths A°	Wavenumbers			Transition v'—v''
	Present Authors	Mahanti	Fergusson	
5275.73	18949.5	18949.2	18951	3—1
5260.94	19002.8	—	—	—
5251.72	19036.2	—	—	8—5*
5240.28	19077.7	—	—	—
5229.94	19121.7	19121.7	19121	2—0
5202.30	19220.3	19220.3	—	7—4
5152.60	19402.3	19402.7	—	6—3
5104.42	19584.4	19586.7	19586	5—2
5056.84	19769.8	19767.9	19768	4—1
5011.34	19949.2	19952.5	19950.0	3—0
4998.30	20001.2	19998.0	—	8—4
4951.01	20192.1	20191.5	20191	7—3
4904.45	20384.0	20385.0	20383	6—2
4858.92	20576.5	20576.7	20578	5—1
4850.19	20612.0	—	—	—
4820.99	20736.9	—	—	—
4812.76	20772.3	20769.1	20773	4—0
4767.57	20969.2	20969.1	—	8—3
4722.11	21175.1	21175.1	—	7—2
4676.43	21378.0	21376.2	—	6—1
4632.70	21579.7	21579.7	—	5—0
4553.94	21953.0	21952.1	—	8—2

*Bands observed for the first time by the authors and fitted into Mahanti's scheme.

With the exception of a few weak bands, almost all the other bands as reported by Fergusson and Mahanti, extending up to λ6590Å on the longer wavelength side, have been recorded on our plates (figure 1). These have been presented in table 1, along with the measurements of Fergusson and Mahanti. Besides these, a large number of new bands have been revealed by our spectrograms. Twenty-nine of them were quite convincing and were degraded to red. These also have been included in table 1. Nine of these new bands can easily be fitted into Mahanti's scheme, extending the system to $v'' = 8$. The corresponding transitions have been shown against their wavelengths in column 5 of the same table and have been
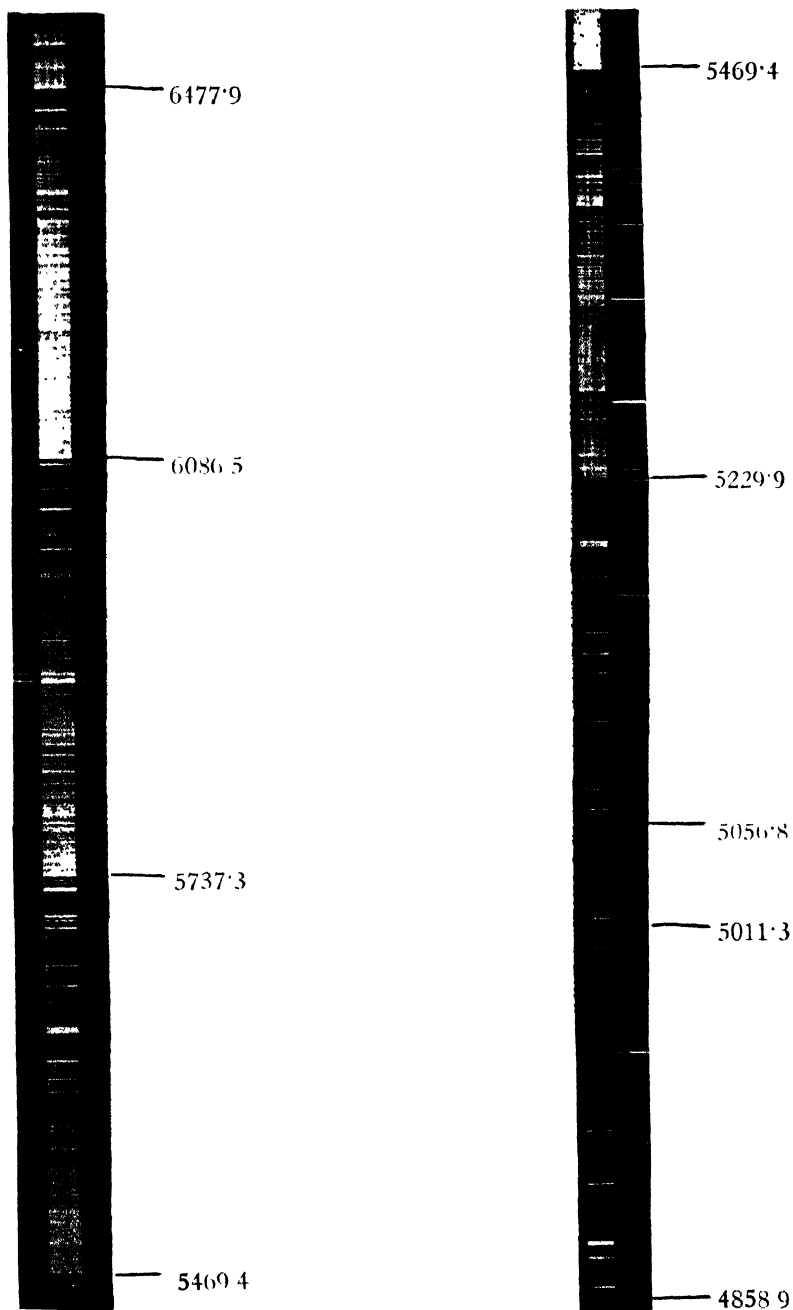
Fig 1. Emission spectrum of VO molecule.

marked with asterisks. The remaining 20 bands could not be fitted into Mahanti's scheme.

Infra-red System

Failure to accommodate these 20 bands in the yellow-green system, naturally led us to an attempt to see whether these bands could form an extension of the infra-red system of Keenan and Schroeder (1952). Keenan and Schroeder determined the vibrational frequency and anharmonicity constants on the basis of eight components for each band. Some of the components on their spectrograms, however, were extremely weak, while the reality of few others was somewhat questionable. Inclusion of such measurements of doubtful character in the calculation, is likely to vitiate the results and hence, we thought it proper to recalculate these constants using only 3 components for each band, which appeared with appreciable intensity on their spectrograms. The values thus calculated have been given in table 2.

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Table 2

Vibrational constants of VO (Infra-red System)

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	ν_e	ω_e'	$\omega_e\chi_e'$	ω_e''	$\omega_e\chi_e''$
Keenan and Schroeder	11,788.1	908.2	5.0	1,012.6	6.3
Calculated by the present authors	12,785.49	909.1	5.0	1,010.0	5.25

Although the values of w_e', $w_e\chi_e'$ and w_e'' calculated by us do not differ much from those obtained by Keenan and Schroeder, the value of ν_e (viz. 12,785.49) differs appreciably from that reported by them (viz. 11,788.1). This, we believe, must be a misprint, since no accord can be obtained between the experimental values and those calculated on the basis of the above value for ν_e. The value 6.3 for $w_e\chi_e''$ obtained by them seems to be too high, particularly in view of the suggestion made by them that the lower state for the infra-red system is the same as that for the yellow-green system, the value of $w_e\chi_e''$ for which, as recently found by Lagerqvist and Selin (1957b), is 4.97. The value 5.25 resulting from our calculations is closer to this value.

None of the new bands observed by us can be fitted into the scheme presented by Keenan and Schroeder, nor could they be fitted into an independent scheme.

Spurious Band-heads

Besides the twenty-nine band heads reported above, a few more appeared to be slightly shaded on the shorter wave-length side. The general appearance of

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these heads was of doubtful nature and one could not be positive about their degradation. However, the following three heads were quite convincingly degraded to the ultra-violet.

16576.8 cm^{-1}, 16943.1 cm^{-1} and 16965.8 cm^{-1}.

There was no systematic variation in intensities of these bands with the increase or decrease of current. They were found to appear somewhat spuriously. Nothing definite, therefore, can be said about their emitter. The only special feature that may be believed to coincide with their occurrence is a greenish-yellow glow in the arc flame and this, in all probability, may be responsible for their production. They are likely to be due to some impurity.

Table 3

Assignment of the unidentified bands reported by Fergusson.

Transition $v'-v''$	Wavenumbers	
	Keenan and Schroeder	Fergusson
0—0	12733.9	—
	12711.0	12710
	12661.2	12661
	12639.3	—
	12620.3	—
	12592.8	12591
	12547.9	—
	12538.8	—
0—1	11736.3	—
	11709.6	11708
	11661.9	11661
	11637.5	—
	11627.6	11625
	11592.4	11595
	11547.6	—
	11535.4	—
1—2	11645.9	—
	11619.7	—
	11568.3	—
	—	11550*
1—1	—	12629*
	12609.8	—
	12558.8	—
	—	12534*
	12525.6	—

Table 3 (*Contd.*)

Transition $v'-v''$	Wavenumbers	
	Keenan and Schroeder	Fergusson
2—2	12538.8	12534
1—0	13631.7	13629
	13611.2	—
	13560.3	13559
	13540.0	—
	13522.2	—…
	13484.1	—
	13445.6	—
	13430.5	13431
2—1	13522.2	13521
	13500.4	13500
	13449.3	13448
	13430.5	—
	13412.6	—
	13379.4	—
	—	13340*
	13322.7	—
3—2	—	13409*
	13344.2	—
	13304.4	13301
	13270.5	—
2—0	—	14503*
	14451.0	—
	—	14411*
	—	14381*
	14336.0	—
	14324.3	—
3—1	14370.1	—
	14324.3	—
	14289.6	14291
	14260.3	14261
	14206.1	—
5—3	14140.7	14139
	14086.9	14082

*Unidentified bands as reported by Fergusson and fitted in Keenan and Schroeder's scheme.

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Table 5 (contd.)

Transition v'-v''	Wavenumbers				O—C Differences in cm^{-1}		
	Observed	Calculated			L & S	Present Authors	Mahanti
		Constants of L & S	Present Authors	Mahanti			
5,0	21579.7	21550.5	21583.33	21582.07	+29.2	− 3.63	− 2.37
5,1	20576.5	20548.8	20583.03	20579.13	+27.7	− 6.53	− 2.63
5,2	19584.4	19557.2	19592.33	19585.95	⏐27.2	− 7.93	− 1.55
5,3	18604.8	18575.5	18611.23	18602.53	+29.3	− 6.43	+ 2.27
5,4	17632.4	17603.6	17639.73	17628.87	⏐28.8	− 7.33	+ 3.53
5,5	16673.1	16641.8	16677.83	16664.97	+31.3	− 4.73	+ 8.13
5,6	15718.0	15690.2	15725.53	15710.83	⏐27.8	− 7.53	+ 7.17
5,7	14775.3*	14748.0	14782.83	14766.45	+27.3	− 7.53	+⏐8.85
6,0	22383.1	22337.2	22382.33	22380.77	+45.9	+ 0.77	+ 2.33
6,1	21378.0	21335.5	21382.03	21377.83	+42.5	+ 4.03	+ 0.17
6,2	20384.0	20343.9	20391.35	20384.65	+40.1	− 7.35	− 0.65
6,3	19492.3	19362.2	19410.73	19400.63	+40.1	− 7.93	+ 1.67
6,4	18428.8	18390.3	18438.73	18427.57	+38.5	− 9.93	+ 1.23
6,5	17466.1	17428.5	17476.83	17463.67	+37.6	−10.73	+ 2.43
6,6	16515.4	16476.5	16524.53	16509.53	+38.9	− 9.13	+ 5.87
6,7	15574.8	15534.7	15581.85	15565.15	+40.1	− 7.05	+ 9.65
7,2	21175.1	21117.4	21180.35	21172.55	+57.7	− 5.25	+ 2.55
7,3	20192.1	20135.1	20204.25	20189.13	⏐56.4	−12.15	+ 2.98
7,4	19220.3	19113.8	19227.75	19215.47	+56.5	+⏐7.45	+ 4.83
7,5	18257.1	18201.9	18265.85	18251.57	+55.2	− 8.75	+ 5.53
7,6	17307.6	17250.4	17313.55	17297.43	+57.2	− 5.95	+10.17
7,7	16367.6	16308.2	16370.85	16353.05	+61.9	− 3.25	+14.55
8,2	21953.0	21877.9	21958.75	21949.65	+75.1	− 5.75	+ 3.35
8,3	20969.2	20896.0	20977.66	20966.23	+68.8	− 8.40	+ 2.97
8,4	20001.2	19924.1	20006.10	19990.57	+77.1	− 4.90	+10.63
8,5	19036.2	18962.3	19044.20	19028.67	+73.9	− 8.00	+ 7.53
8,6	18086.7	18010.7	18091.40	18074.53	+76.0	− 4.70	+12.17
8,7	17145.4	17068.5	17149.30	17130.15	+76.9	− 3.90	+15.25
8,8	16211.9	16136.3	16217.57	16195.53	+75.6	− 5.67	+16.37

The vibrational constants estimated by drawing ΔG_v : v curves based on our data have been presented in table 4 along with those of Mahanti and Lagerqvist and Selin. The wave numbers of bands calculated using these constants, are given in column 4 of table 5 and the deviation in column 7 of the same table. The wave numbers give fairly good agreement with the observed ones as will be seen from column 7. The calculated wave numbers and the deviations

obtained using Mahanti's data are given in columns 5 and 8 respectively. It will be observed that the agreement in the case of our values is a shade better than that with Mahanti's.

Lagerqvist and Selin have determined the constants corresponding to the lower state with considerable accuracy. Our values do not differ much from these. They do not, however, emphasize on the accuracy of the values of the upper state. These, we believe, need be revised.

The work reported in this paper was carried out in the Spectroscopic Laboratories, Department of Physics, University of Poona, when the authors were working there.

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