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Emission spectroscopy of a new $^2\Delta$–$1^2\Delta$ system of VO

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Abstract

High-resolution spectra of VO have been reinvestigated in the 12000–31000 cm^{-1} region. VO was produced in a vanadium hollow cathode lamp by discharging 1.5 Torr of Ar and the spectra were recorded using a Fourier transform spectrometer. The oxygen needed to produce VO was present in the system as an impurity. Three new bands observed in the 21000–22100 cm^{-1} region have been attributed to a new $^2\Delta$–$1^2\Delta$ electronic transition of VO. Two bands, with origins near 21044 and 22038 cm^{-1}, have been assigned as the 0–1 and 0–0 bands of the $^2\Delta_{3/2}$–$1^2\Delta_{3/2}$ sub-band while a weak band with an origin near 21975 cm^{-1} has been assigned as the 0–0 band of the corresponding $^2\Delta_{5/2}$–$1^2\Delta_{5/2}$ sub-band. A rotational analysis of these sub-bands has been obtained and spectroscopic constants have been extracted. The $1^2\Delta$ state is known from the previous analyses of the doublet transitions of VO in the near infrared. The present observation has allowed the determination of the vibrational interval $\Delta G_{1/2}$ and the equilibrium rotational constants for the $1^2\Delta_{3/2}$ state.

Keywords: Emission spectroscopy; Fourier transform spectroscopy

1. Introduction

VO is a molecule of astrophysical importance [1–5]. The electronic spectra of the VO radical appear from the near infrared to the visible in absorption spectra of many cool stars, and provide the basis for the spectral classification of late M-type stars [5]. These spectra have been utilized as a sensitive probe of the circumstellar environment and are of significant importance in modeling of the stellar atmospheres. VO and other oxides of vanadium are also of chemical and industrial importance because of their use in optical devices, semiconductors, catalysts, and coatings [6–11].

VO is the most extensively studied molecule in the group 5 oxide family. The ground state of VO is well established as a $^4\Sigma^-$ state from numerous theoretical [12,13] and experimental [14–21] studies. Three strong transitions of VO have been identified in the near infrared and visible regions which have been assigned as the $A^4\Pi$–$X^4\Sigma^-$ [14], $B^4\Pi$–$X^4\Sigma^-$ [15–17], and $C^4\Sigma^-$–$X^4\Sigma^-$ [18,19] transitions, all involving the ground state as the lower state. Two more quartet–quartet transitions of VO have been identified in the near infrared that originate from the $D^4\Delta$ state and terminate on the $A^4\Pi$ state and another low-lying $A'^4\Phi$ state [20]. The near infrared region also consists of several doublet–doublet transitions [20]. Among the doublet transitions of VO, there are two $^2\Pi$–$^2\Delta$ transitions near 7200 and 8126 cm^{-1} having a common $^2\Delta$ lower state which will be referred in this paper as the $1^2\Delta$ state. Recently another near infrared transition, $^2\Phi$–$1^2\Delta$, has been identified near 5500 cm^{-1} having its lower state in common with the two doublet–doublet transitions mentioned above [21]. There is a fourth doublet transition, which has been assigned as $2^2\Delta$–$1^2\Phi$, that does not have any state in common with the other doublet transitions [20]. The location of these doublet states is not known with any

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precision relative to the ground state since the quartet and doublet transitions do not have any state in common.

In the current work we have identified a new $^2\Delta$–$1^2\Delta$ transition of VO in the 21 000–22 100 cm^{-1} region having its lower state in common with the lower $1^2\Delta$ state of three of the four known doublet transitions. In this paper we report the rotational analysis of the 0–1 and 0–0 bands of the $^2\Delta_{3/2}$–$1^2\Delta_{3/2}$ sub-band and the 0–0 band of the $^2\Delta_{5/2}$–$1^2\Delta_{5/2}$ sub-band. From this analysis we have determined the fundamental vibrational interval and equilibrium rotational constants for the $1^2\Delta_{3/2}$ state.

2. Experimental details

The new VO bands were identified in an archival spectrum of vanadium recorded in 1979 at the National Solar Observatory at Kitt Peak by W. Whaling and J.W. Brault. The molecules were excited in a hollow cathode lamp and the spectra were observed using the Fourier transform spectrometer associated with the McMath–Pierce telescope of the National Solar Observatory at Kitt Peak. The vanadium cathode lamp was operated at a current of 300 mA with a flow Ar at a pressure of 1.5 Torr. The spectrometer was equipped with a UV beam splitter, midrange silicon photodiode detectors, and TC497 and WG345 filters. The spectra were recorded at 0.042 cm^{-1} resolution by coadding 10 scans in about 70 min of integration.

The spectral line positions were extracted 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 feature. In addition to VO, the V and Ar atomic lines were also present in this spectrum. The spectra were calibrated using the measurements of the Ar atomic lines [22]. The absolute accuracy of the wavenumber scale is expected to be of the order of ± 0.005 cm^{-1}. The new bands are very weak in intensity compared with other known transitions of VO. The strong rotational lines of the new transition appear with a typical signal-to-noise ratio of 4:1 and have an approximate line width of 0.032 cm^{-1}. The precision of measurements of strong and unblended lines of VO is expected to be better than ± 0.005 cm^{-1}.

3. Results and discussion

This spectrum consists of a number of VO bands belonging to the $C^4\Sigma^-$–$X^4\Sigma^-$ transition, although no oxygen was added to the discharge. The oxygen atoms required to produce VO were probably present in the system as an impurity. We were able to identify the 0–1, 0–0, 1–0, 2–0, and 3–0 bands of the $C^4\Sigma^-$–$X^4\Sigma^-$ transition along with several sequence bands involving higher vibrational levels of the upper and lower states. After a careful examination of this spectrum we noted the presence of three additional weaker bands with R heads near 21 050, 21 979, and 22 042 cm^{-1}. These bands consist of two branches and do not belong to any known transitions of VO. A rotational analysis of these bands indicated that the bands at 21 050 and 22 042 cm^{-1} had a common upper state but the lower state constants for these two bands matched with the rotational constants of the $v'' = 1$ and $v'' = 0$ vibrational levels of the $1^2\Delta_{3/2}$ state, while the band at 21 979 cm^{-1} had a lower

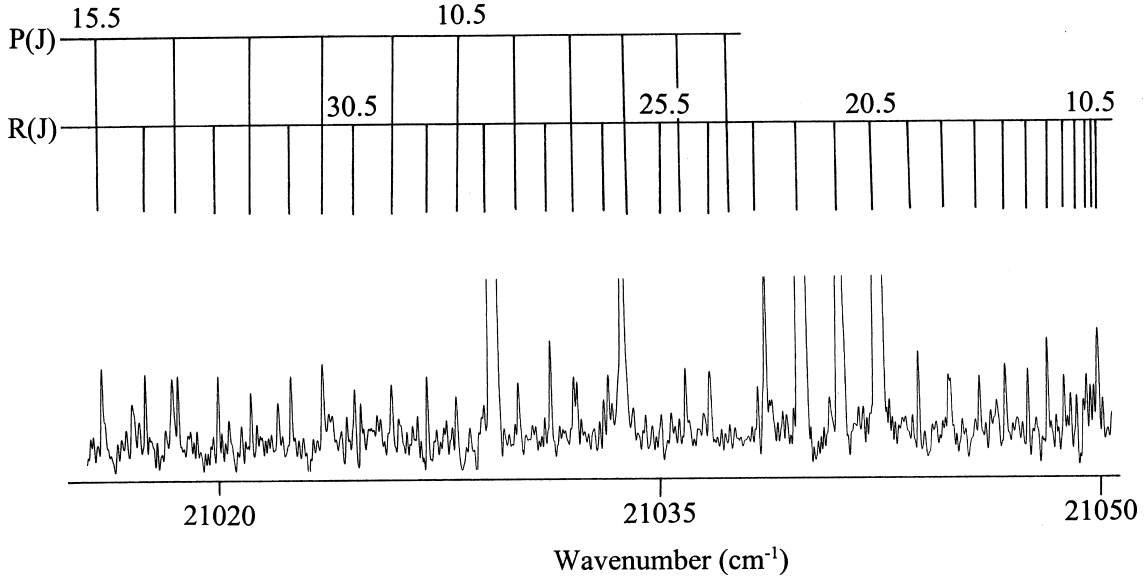

Fig. 1. An expanded portion of the 0–1 band of the new $^2\Delta_{3/2}$–$1^2\Delta_{3/2}$ system of VO near the R head.