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LETTERS TO THE EDITOR

Excited Molecular States and Bonds in the Structures of Vanadium Oxides

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A study of the oxygen thermoemission activity of samples of vanadium oxides and oxovanadium series of Magneli phases (V_nO_{2n-1}, $n = 4$–8; these phases were identified by X-ray diffraction and gas pycnometry) by gas chromatography, IR spectrophotometry, and adsorption–desorption calorimetry (qualitative and quantitative analysis of the molecular composition of the desorbed gas mixture) showed that the prevailing species in the desorbed mixture are electronically excited oxygen molecules in the $^1\Delta_g$ and $^1\Sigma_g^+$ states (30–60%). The thermal desorption of oxygen is irreversible. In this work, we studied the structural nature of this effect by high-temperature high-resolution IR spectroscopy (IKS-25M).

The spectrum of vanadium(V) oxide recorded at room temperature in a dry air atmosphere contains in the region of stretching vibrations of the V–O bond in the ground state ($^4\Sigma^-$, ~1000 cm^{-1}) a strong absorption band with a maximum at 1020 cm^{-1} and a shoulder at 1000 cm^{-1} with an extended long-wave wing. The absorption at 1000–900 cm^{-1} is assignable to a series of vibrational transitions in the lowest excited state of the V–O bond. The band at 900–750 cm^{-1} well agrees with published data on the vibration frequencies of electronically excited states ($^4\Sigma^-$, $^4\Pi_{(r)}$) of this bond [1, 2].

A strong maximum at 1020 cm^{-1} is due to the increased content of O_3^- groups [3]. Strong bands of hydroxy groups involved in hydrogen bonds (3685, 3668 cm^{-1}) [4] are also indicative of the presence of O_3^- groups. Strong peaks of emission at 302 cm^{-1} and absorption at 280 cm^{-1} engage attention. The absorption in this range is due to the presence of negatively charged molecular oxygen species and formation of relatively weak O–O bonds in their oligomerization [3].

The oxygen–oxygen bonds in uncharged molecular species give rise to a strong vibrationally excited singlet of the ground state (1558 cm^{-1}), a series of its vibrational transitions (1540, 1507, 1490, 1470 cm^{-1}), and strong absorption bands of electronically excited states (1457, 1405–1200 cm^{-1}). The strong emission and absorption peaks at 1650 and 1682 cm^{-1} can be assigned to oligomeric oxygen species [3].

The spectrum also contains medium well-resolved absorption bands at 1866, 1842, and 1827 cm^{-1}, which, along with the absorption at 1000 cm^{-1}, suggest the presence of molecular radical ions O_2^+ [3].

A decrease in the oxidation state of the cation in going to V_2O_4 is accompanied by disappearance of the absorption band at 1020 cm^{-1} and appearance of a characteristic group of strong bands in the range 1075–1030 cm^{-1}, suggesting the presence of neutral ozone molecules [3]. The vibrations of the core bonds give rise to a series of narrow bands in the range 1000–830 cm^{-1}, with the bands at 1000–970 and 900 cm^{-1} being the strongest. Also, strong bands of peroxy groups appear at 667, 502, and 420 cm^{-1} [5], and the bands of their supramolecular bonds, at 282, 275, and 255 cm^{-1} [6].

A CNDO simulation [7] of the vibrational activity of the V–V bond (2.619 Å) shows that this bond should give a weak singlet at ~380 cm^{-1}. In the spectrum of V_2O_4, there is a group of medium bands in the range 360–320 cm^{-1}, and in the spectrum of V_2O_5 there are weak absorption maxima at 360, 350, and 340 cm^{-1}.

The spectrum of vanadium(V) oxide at 673 K exhibits a well-resolved pattern of core vibrations, with strong absorption bands at 1000 and 900 cm^{-1}; the ratio of their optical densities suggests prevalence of the electronically excited states of the V–O bonds. The first excited state, $^4\Pi_{(r)}$, is manifested most strongly, giving a doublet at 902 and 907 cm^{-1}. The second electronically excited state, $^4\Sigma^-$, gives a less strong absorption band with the center of gravity at 853 cm^{-1}.

An increased content of peroxy groups is detected. They give strong emission and absorption peaks in the range 860–400 cm^{-1}. This assignment is confirmed by significant growth of absorption in the range of OH vibrations at 3680–3560 cm^{-1}.

At 873 K, the absorption in the range 1200–1000 cm^{-1} becomes virtually 100%. Maxima at 1175 and 1092 cm^{-1} become characteristic features. The peroxy groups are manifested as more structured absorption with strong maxima at 667 and 540–500 cm^{-1}. Detection of a strong vibrationally excited band at 3620 cm^{-1} (O–O–H) is quite consistent with these observations. The peaks at 3685 and 3645 cm^{-1} show that the concentration of ozone-like oxygen oligomers remains high [4].

The intensity of absorption bands at 302 and 280 cm^{-1} increases by a factor of 3.

The content of metal–metal bonds remains approximately the same, as indicated by insignificant changes in the intensities of the absorption bands at 370, 358, and 323 cm^{-1}.

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