Theoretical Characterization of the Ground and Optically Excited States of α'-NaV_2O_5

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The character of the ground and optically excited states was investigated by quantum chemical calculations. We propose a rung ground state with V $3d_{xy}^1$-O $2p_y^1$-V $3d_{xy}^1$ character, instead of the conventional picture of one unpaired electron shared by 2 V ions. The unpaired electron on O is low-spin coupled to the V d electrons and spin density is predicted to be localized on vanadium. The absorption peak at 0.9 eV is assigned to a state with similar orbital occupations but a different spin coupling scheme, resulting in spin density localized on the bridging oxygen.

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The physical properties of α'-NaV_2O_5 have generated much debate over the last few years. In this material the V ions, each roughly situated in the center of a VO_5 pyramid, form layers in which one-dimensional vanadium chains are arranged in a network of two-leg ladders. Within the same ladder the VO_5 pyramids share the corners of their bases, whereas pyramids on adjacent ladders point alternately up and down with respect to the basal plane and are linked by common edges. Early x-ray diffraction (XRD) measurements at room temperature reported two inequivalent sets of vanadium sites, with alternating magnetic V^{4+} ($S = 1/2$) and nonmagnetic V^{5+} ($S = 0$) chains [1]. Above 34 K the temperature dependency of the magnetic susceptibility is indeed consistent with that of a $S = 1/2$ antiferromagnetic (AF) Heisenberg chain [2,3]. The rapid decrease of the susceptibility below 34 K [2], a lattice distortion [4], and the spin gap behavior [4] were then assigned to a spin-Peierls transition, where dimerization of the V^{4+} ions occurs. However, further XRD [5,6] and nuclear magnetic resonance (NMR) [7] experiments have shown that at high temperature (HT) all V ions are equivalent, and the model proposed in Ref. [1] was questioned. Density functional (DF) [6] and model Hamiltonian [6,8] studies led to a different picture, based on parallel quasi-one-dimensional AF spin chains with a spin of 1/2 per rung of the ladder, in a V-V bonding molecular orbital.

NMR [7,9] and XRD [10–12] data suggest that the phase transition at 34 K is also coupled with charge ordering (CO) within the vanadium layers. Nevertheless, the low temperature (LT) structure remains controversial.

In this Letter, we report results of *ab initio* quantum chemical embedded cluster calculations of the electronic structure of NaV_2O_5 in the HT phase. Our analysis shows that the 2 V $3d_{xy}$ orbitals and also the bridging O $2p_y$ of a V-O-V rung have each a population of about one electron, in contrast to previous models [6,8] which assumed a closed O $2p$ shell and a single V d electron per rung of the ladder. Based on this new picture of the electronic ground state (GS) we also propose a different interpretation of the peaks observed in the optical absorption spectrum.

Our study is structured into two sections. The nature of the GS and of the low-energy onrung excitations were first determined by complete active space self consistent field (CASSCF) calculations [13,14] on embedded $[V_2O_9]^{9-}$ clusters including two VO_5 pyramids on the same rung; see Fig. 1. Second, magnetic couplings between spins on adjacent rungs were estimated by second order perturbation (PT2) calculations [14,15] on $[V_4O_{16}]^{14-}$ clusters.

The crystalline environment is modeled by an array of point charges (PCs) at the lattice positions. In agreement with previous calculations [16,17] we find that the apical oxygen O_A is covalently bonded to the V atom and in the valence state O^-. As explained below, our analysis shows that the bridging oxygen on the rung of the ladder, O_R, has an effective charge close to -1.0 as well. Therefore we represent the $O_{A,R}$ and V ions by $-1.0e$ and $+3.0e$ PCs, respectively, whereas the other oxygens and the Na ions are modeled by their formal charges, $-2.0e$ and $+1.0e$. At the boundaries of this array we put a set of PCs optimized to fit the Madelung potential in the cluster region. To avoid artificial polarization of the cluster orbitals towards the neighboring positive PCs, the nearest V and Na cations are described by total ion potentials

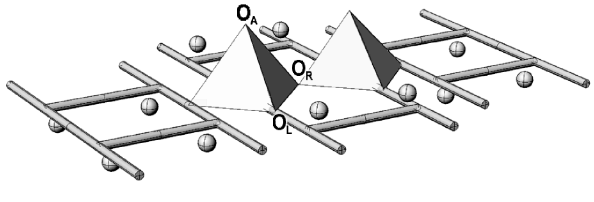

FIG. 1. Schematic representation of the $[V_2O_9]$ cluster, with the V ions inside the oxygen pyramids. Gray spheres represent neighboring V sites. The ladders are a guide for the eye.

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(TIPs) [18]. Atomic natural orbital Gaussian-type basis sets have been applied: V $(21s15p10d6f)/(6s5p4d2f)$ and O $(14s9p4d)/(4s3p2d)$ in the $[V_2O_9]$ cluster; V $(21s15p10d)/(5s4p3d)$ for vanadium, O $(14s9p4d)/(4s3p1d)$ for the bridging oxygens, and O $(14s9p)/(3s2p)$ for the others in the larger $[V_4O_{16}]$ cluster, including two adjacent rungs [19]. We have used the crystal structure as determined by Meetsma *et al.* [5].

NaV_2O_5 is isostructural to the spin-ladder material CaV_2O_5. NMR measurements [20] and DF calculations [21] indicate that in CaV_2O_5 the unpaired d electron of each V ion occupies the xy orbital, where the x and y directions are, respectively, along the a and b axes of the $Pmmn$ reference system. Intraladder AF interactions occur through the π overlap of V $3d$ and O $2p$ orbitals. The V-O distance across the rung is shorter than along the leg, leading to stronger V $3d$–O $2p$ coupling across the rung. Also the tilt of the VO_5 pyramids increases the d_{xy}-p_y-d_{xy} overlap across the rung. The picture proposed for CaV_2O_5 consists of rung singlets with strong interaction inside the V-O-V unit supplemented by weak AF correlations along the legs of the ladder [21]. Substitution of the Ca^{2+} ions with Na^+ reduces the number of valence electrons on each V-O-V rung. We are able to show that a realistic model for NaV_2O_5 should explicitly include not only the V $3d_{xy}$ orbitals but also the O_R $2p_y$.

Relative energies of states where the $2p_y$ orbital has either single or double occupation are depicted in Fig. 2. Remarkably, one-configuration restricted open-shell Hartree-Fock (ROHF) calculations predict that the lowest state is a quartet (leftmost column). This state has A_2 symmetry in the C_{2v} cluster point group, and originates from the $p^1d_+^1d_-^1$ configuration. d_+ and d_- are essentially the plus and minus combinations of the two d_{xy} orbitals, with some d_{zy} character mixed in, and transform according to the A_2 and B_2 irreducible representations, respectively, whereas p has mostly O_R $2p_y$ character and belongs to B_2. These orbitals also reflect modest d_{xy}-p_y-d_{xy} covalent bonding. Thus, p has a small bonding V $3d_{xy}$ contribution and d_- has a small antibonding O_R $2p_y$ contribution.

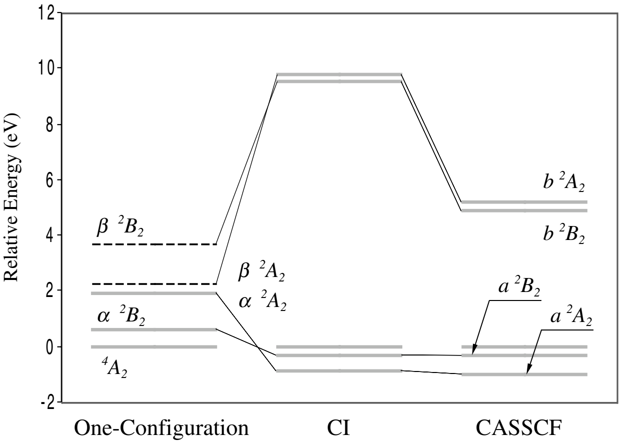

FIG. 2. p^1 and p^2 states by one-configuration, CI, and CASSCF calculations. The states in the leftmost column correspond to: $^4A_2$ $(|pd_+d_-|)$, α $^2B_2$ $(\,|\,pd_+\bar{d}_+\,|-|\,pd_-\bar{d}_-\,|\,)$, α $^2A_2$ $(\,|\,pd_+\bar{d}_-\,|\,)$, β $^2A_2$ $(\,|\,p\bar{p}d_+\,|\,)$, and β $^2B_2$ $(\,|\,p\bar{p}d_-\,|\,)$. The CI was performed in terms of orbitals optimized for $^4A_2$.

The lowest doublets, α $^2B_2$ and α $^2A_2$, are 0.6 and 1.9 eV above the $^4A_2$ state and result from p^1 configurations as well. Strictly speaking, these two states are not ROHF solutions. They were obtained from small configuration-interaction (CI) calculations which also included the p^0 configurations, and are expressed in terms of high-spin orbitals. The contribution of the p^0 configurations is, however, negligible, since the p^0 configuration state functions have much higher energy. In addition, we show below that the use of orbitals optimized for the $^4A_2$ state is not a severe approximation for the lowest two doublets.

In terms of localized orbitals, V $3d_{xy}$ and O_R $2p_y$, the lowest three states arise from the d_{xy}^1-p_y^1-d_{xy}^1 configuration. Horsch and Mack [8], and Smolinski *et al.* [6] associated the GS of the V-O-V rung to a p^2 configuration where the single d electron occupies a d_{xy}-d_{xy} bonding orbital. ROHF situates the lowest p^2 state, β $^2A_2$ $(p^2d_+^1d_-^0)$, at 2.3 eV above the quartet $^4A_2$ $(p^1d_+^1d_-^1)$. The other p^2 state, β $^2B_2$ $(p^2d_+^0d_-^1)$, involves a different occupation of the d orbitals and has a relative energy of 3.7 eV with respect to $^4A_2$. The peak at 0.9 eV in the optical absorption was assigned to such a transition between linear combinations of d_{xy} orbitals [22]. It is important to note that the ROHF relative energies of the p^2 states, the dashed lines in Fig. 2, have only a limited meaning. Since these wave functions are optimized without restricting them to be orthogonal to the p^1, or α, states, the two doublets in both A_2 and B_2 symmetry have mutual overlaps, 0.28 and 0.08, respectively. Orthogonalization of β $^2A_2$ to α $^2A_2$ and β $^2B_2$ to α $^2B_2$ increases the energies of the β states by about 2 and 0.2 eV.

The correct energy ordering can be obtained only by going beyond the one-configuration picture. The p^1-p^2 CI causes large differential energetic effects and yields a doublet $^2A_2$ GS. This is depicted in the second column of Fig. 2. Here the CI was performed in terms of orbitals optimized for high-spin coupling. The mixing between the p^1 and p^2 configurations turns out to be rather modest for the B_2 states—the CI weights (squares of the CI coefficients) are 0.90 and 0.10. It is, however, more important for the A_2 states, with weights of 0.74 and 0.26, inducing considerable separation between the CI energies. The separate optimization of the orbitals for each state by CASSCF calculations causes minor energy lowerings for the lowest $^2A_2$ and $^2B_2$ doublets (rightmost column of Fig. 2). On the other hand, for the higher p^2 states, for which the $^4A_2$ orbitals lead to an improper representation, large relaxation effects of 4–5 eV occur.

Table I lists relative energies, Mulliken populations (MPs), and spin MPs of the V d_{xy} and the O_R p_y atomic basis functions for the lowest A_2 and B_2 roots. It is well known that MPs are basis set dependent. Still, differences in populations for different states give valuable qualitative insight in the character of the wave functions. The electron

TABLE I. Charge and spin MPs of the V $3d_{xy}$ and O_R $2p_y$ atomic basis functions for the lowest A_2 and B_2 states. CASSCF results with three electrons and three orbitals in the active space. The spin MPs are for maximum M_s.

State	$a\ ^2A_2$	$a\ ^2B_2$	$^4A_2$	$b\ ^2B_2$	$b\ ^2A_2$
Rel. En. (eV)	0	0.7	1.0	6.1[a]	6.5[a]
MP[b]:					
V $3d_{xy}$	1.7	1.8	1.8	1.1	1.2
O_R $2p_y$	1.0	1.0	1.0	1.8	1.7
Spin MP[b]:					
V $3d_{xy}$	1.2	0.0	1.9	0.7	1.1
O_R $2p_y$	-0.3	1.0	1.0	0.2	-0.1

[a] The b roots were optimized with $b : a$ ratios of 2 : 1.
[b] The $3d$ MPs are summed over the 2 V ions.

populations of each V d_{xy} and of the O_R p_y are essentially the same for $a\ ^2A_2$, $a\ ^2B_2$, and $^4A_2$, 0.8–0.9 and 1.0, respectively. In contrast, the spin MPs show important differences. According to our calculations the GS of the V-O-V rung has predominant d^1_{xy}-p^1_y-d^1_{xy} character. It corresponds to a spin doublet where the spins in the p and antibonding d_- orbitals are low-spin coupled. The excited state at 0.7 eV implies a different spin coupling scheme: the d electrons are coupled to a singlet, and the spin on the bridging oxygen is doublet coupled to it. The $a\ ^2A_2$–$a\ ^2B_2$ splitting is in reasonable agreement with the 0.9 eV excitation in the optical absorption [22]. We assign this peak to the $a\ ^2A_2 \rightarrow a\ ^2B_2$ transition.

The results in Fig. 2 and Table I were obtained by calculations with three active orbitals. This is the minimal active space which still includes the O_R $2p_y$. To investigate whether our results for the character and ordering of the lowest states are also obtained with more accurate wave functions, we repeated the calculations with a larger active space. Analysis of the cluster wave functions shows that the $2p$ orbitals of the apex oxygens have significant V $3d$ character mixed in, reflecting V-O_A covalent bonding. The best choice to extend the active space is then to add the O_R $2p_x$ and $2p_z$, all six O_A $2p$ orbitals, plus the V $3d$ z^2, zy, zx, and x^2-y^2 virtuals.

Single and double excitations from the O_R $2p_x$, $2p_z$, and O_A $2p_x$, $2p_y$, $2p_z$ orbitals were considered by applying the restricted active space (RAS) method [23]. We used CAS reference wave functions based on an active subspace including the O_R $2p_y$ and V $3d_{xy}$ orbitals. The other V $3d$ components formed an orbital subspace allowed to be occupied with up to two electrons. The $a\ ^2A_2$–$a\ ^2B_2$ splitting becomes now 1.0 eV. Excitation energies and results of MP analysis for the lowest two $^2B_2$ states are shown in Table II. Composition of the cluster wave functions and the MPs indicate that $b\ ^2B_2$ is the effect of a metal to O charge transfer (CT) excitation, namely, V $3d_{xy}$ to O_R $2p_y$. This state can explain the 3.3 eV peak in the x-polarized absorption. However, our calculations predict a relative energy of 5.4, about 2 eV higher. Probable sources of this discrepancy are the partial neglect of dynamical correlation and of electronic relaxation effects in the crystal as response to the CT process. These latter effects were investigated by increasing the size of the cluster. The ions added were the nearest four Na and ten O neighbors, supplied with $(14s9p4d)/(3s2p1d)$ basis functions. Since the V ions are not very polarizable, the closest vanadiums were still represented by TIPs. We found that the relative energy of the $b\ ^2B_2$ state is lowered by 0.4 eV. It is expected to be lowered further when longer-range polarization effects are included.

Several states of $^2B_2$ symmetry were found at 1.5–3.5 eV above the $b\ ^2B_2$ root, mainly arising from O_A $2p$ to V $3d$ CT configurations. The calculated transition dipole moments denote that within these CT-like states most of the intensity is carried by those connected to $p_y \rightarrow d_{zy}$ excitations. This is due to the mixing between d_{xy} and d_{zy} orbitals. We assign such O_A to V CT excitations to the feature above 4.0 eV in the optical absorption.

The sensitivity of our results to the magnitude of the Madelung potential was investigated by modifying the size of the embedding charges. First, we utilized the formal charges of a fully ionic model, $V^{4.5+}$, O^{2-}, and Na^+, second, the charges above were divided by two; and third, the embedding was removed completely. The character and ordering of the lowest states were unchanged. With the fully ionic embedding, the minimal CAS $a\ ^2A_2$–$a\ ^2B_2$ and $a\ ^2A_2$–$^4A_2$ excitation energies are still 0.7 and 1.0 eV, as in the original embedding. With half charges these energies are 0.6 and 0.9; without embedding they are 0.5 and 0.7 eV.

It has been found that in NaV_2O_5 the HT magnetic susceptibility is well described by a $S = 1/2$ AF Heisenberg chain model. Fits of $\chi(T)$ led to an exchange constant along the b axis of -560 K in Ref. [2] and -529 K in [3]. The HT theoretical estimates are spread over a wide range, from approximately -900 K by DF and model Hamiltonian studies [6,8] to -58 K by embedded cluster CI calculations [17]. In Ref. [17] the coupling parameter in the b direction has been evaluated by calculations on a $[V_2O_9]$ bipyramidal cluster including 2 V sites

TABLE II. Charge and spin MPs for the $^2A_2$ GS and the lowest two $^2B_2$ excited states. RASSCF results with single and double excitations from the O_R and O_A $2p$ shells. The spin MPs are for maximum M_s.

State	$a\ ^2A_2$	$a\ ^2B_2$	$b\ ^2B_2$
Rel. En. (eV)	0	1.0	5.4[a]
MP[b]:			
V $3d_{xy}$	1.6	1.7	1.1
O_R $2p_y$	1.1	1.0	1.7
Spin MP[b]:			
V $3d_{xy}$	1.2	0.1	0.6
O_R $2p_y$	−0.3	0.9	0.3

[a] The b root was optimized with a $b : a$ ratio of 2 : 1.
[b] The $3d$ MPs are summed over the 2 V ions.

on the same leg. Here we present results of CASPT2 calculations on a $[V_4O_{16}]$ cluster including two adjacent rungs. The Heisenberg exchange constant was extracted from the energy eigenvalues of the singlet and triplet states arising, respectively, from low- and high-spin coupling of the $S = 1/2$ effective spins associated to each of the two rungs: $J = E_S - E_T$. CASSCF wave functions were constructed with an active space that includes the V $3d_{xy}$ and O_R $2p_y$ magnetic orbitals, plus $2p$ orbitals of the oxygens on the legs of the ladder, O_L. These are the bridging $2p_x$ and $2p_z$, which mediate the superexchange, and a set of correlating virtuals of the same symmetry character, referred to as O_L $2p_x^\prime$ and $2p_z^\prime$. In the subsequent CASPT2 calculation all V $3s$, $3p$, $3d$, and O $2s$, $2p$ electrons are correlated. Recent studies have established that such a CASSCF/CASPT2 approach gives accurate estimates of the magnetic couplings for several Ni and Cu ionic insulators [24] and for the spin-ladder vanadate CaV_2O_5 [25]. To exclude so-called intruder states we applied the shift technique proposed in [26]. Shifts in the energy denominators were introduced ranging from 0.24 to 0.32 a.u.; the resulting J ranges from -560 to -515 K, with lower values for higher shifts. Although some degree of uncertainty is contained in our result, rather good agreement is found with the estimates of Refs. [2,3].

NMR [7,9] and XRD [10–12] data indicate that at least two inequivalent V sites exist below 34 K. This inequivalency is usually associated to a CO process. We investigated the LT electronic structure by calculations on clusters of two different geometries, corresponding to the $Fmm2$ system proposed by Bernert *et al.* [10] and to the $A112$ configuration reported by Sawa *et al.* [11]. For both lattice systems we found that the GS and the first excited state have O_R $2p_y^1$ character, as in the HT geometry. The a $^2A_2$–a $^2B_2$ splitting changes by about 0.1 eV, in agreement with the shift observed experimentally, ≈ 0.03 eV [27]. A detailed analysis of the electronic structure below 34 K will be presented in a forthcoming paper.

A strong contribution of the O_R $2p_y^1$ configuration in the GS wave function was previously pointed out by van Oosten [16] and by Suaud and Lepetit [17,28]. In this Letter, we provide evidence that the doublet GS of the V-O-V rung has actually predominant d_{xy}^1-p_y^1-d_{xy}^1 character. By first principles electronic structure calculations, it is shown that such a model is able to explain the main features of the optical absorption, and the AF interaction along the b axis. We attribute the peak at 0.9 eV to a state characterized by a different spin coupling scheme among the valence V $3d_{xy}$ and O_R $2p_y$ electrons; the features above 3 eV are tentatively assigned to V $3d_{xy} \rightarrow O_R$ $2p_y$ and O_A $2p_y \rightarrow$ V $3d_{zy}$ CT excitations. Our analysis suggests that the HT magnetic structure can still be described by a spin model similar to that proposed by Horsch and Mack [8], with an effective $S = 1/2$ spin on each V-O-V rung.

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