

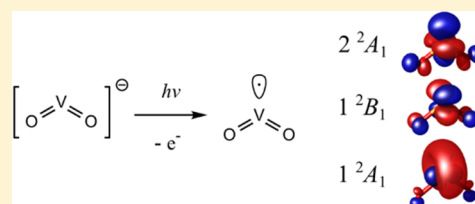
Assignment of Electronic Bands in the Photoelectron Spectrum of the VO_2^- Anion

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ABSTRACT: Assignments of electronic bands in the high resolution photoelectron spectrum of the VO_2^- anion obtained via slow electron velocity-map imaging are discussed in light of a recent theoretical paper that questioned them and proposed an alternate assignment.



The photoelectron spectrum of the VO_2^- anion is complex, since both anionic and neutral VO_2 have multiple low-lying electronic states.¹ The conventional photoelectron spectrum of the anion was reported by Wang and co-workers in 1998.² Our laboratory recently reported a considerably higher resolution spectrum³ using slow electron velocity-map imaging (SEVI) of cryogenically cooled anions.⁴ A recent paper by Hendrickx and Tran⁵ presents an alternative analysis of the conventional photoelectron spectrum and the SEVI spectrum of VO_2^- . One of the main conclusions of Hendrickx and Tran is that the assignment of electronic bands in the experimental SEVI paper is incorrect. They claim that we assigned the lowest-energy band to a photodetachment transition that violates the “one-electron rule”, which states that the photodetachment is fully allowed only to those neutral states whose molecular orbital configuration differs from that of the anion by a single electron. In this Letter, we offer additional support for our assignment based on electronic structure calculations and experimental considerations.

The SEVI spectrum of VO_2^- comprises three electronic bands labeled X, A, and B, in order of increasing electron binding energy. Bands X and A overlap but are fully vibrationally resolved, while band B occurs about 0.8 eV higher. Based on our electronic calculations and Franck–Condon simulations, we assigned the SEVI spectrum according to the scheme on the left-hand side of Figure 1. Bands X, A, and B are assigned to transitions from the \tilde{X}^3B_1 ground state of VO_2^- to the \tilde{X}^2A_1 , \tilde{A}^2B_1 , and \tilde{B}^2A_1 states of VO_2 , respectively. In this scheme, bands X and A are one-electron allowed, involving removal of an electron from the $4b_1$ and $10a_1$ orbitals, respectively. Band B, at higher energy, is not one-electron allowed and was attributed to configuration interaction mixing between the neutral \tilde{X}^2A_1 and \tilde{B}^2A_1 states.

The Hendrickx paper agrees with our assignment of the \tilde{X}^3B_1 state as the anion ground state and with our assignment of band A. However, it disagrees with our assignment of band X, claiming that it is not a one-electron transition and implying that we did not consider this issue in making our assignment. As an example, “...the vibrational X progression was assigned to

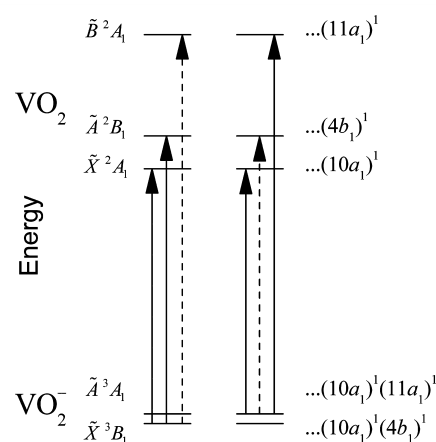


Figure 1. Energy level diagrams and molecular orbital occupancies for low-lying states of VO_2^- and VO_2 (adapted from ref 3). Arrows from left to right on the left-hand diagram show our assignments of bands X, A, and B in the SEVI spectrum. Solid lines represent one-electron transitions.

the electronic $^3B_1 \rightarrow ^2A_1$ transition, which rather surprisingly is not a one-electron detachment process. The multireference character of these states was invoked to explain this assignment but was not proven.” Instead, they assign band X to the $\tilde{A}^3A_1 \rightarrow \tilde{X}^2A_1$ transition shown in Figure 1. Given the content of Figure 1, it is clear that we did not deliberately assign Band X to a forbidden photodetachment transition, in direct contradiction to the oft-repeated statement in the Hendrickx paper. Moreover, at no point in our paper did we invoke a multireference argument to explain our assignment of band X, although we did show that such effects could explain band B, and presented numerical results in support of this argument, which would seem to constitute “proof”.

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In light of these considerations, we present more details from electronic structure calculations to test the validity of our band assignment. We first examine the relevance of the one-electron rule. This is an approximation that arises from Koopman's theorem. To first order, the neutral states generated by photodetachment result from removing single electrons out of various anion molecular orbitals, and thus if a neutral state is not accessible in this way from the anion, it does not appear as a band in the photodetachment spectrum. This picture breaks down when there is significant electron correlation or when the anion and neutral orbitals are not aligned. Figure 2 shows our

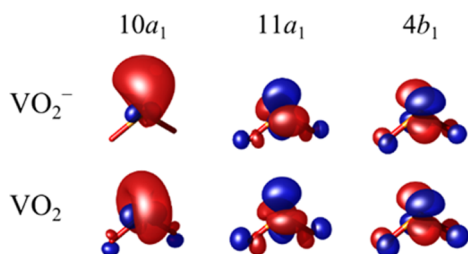


Figure 2. Relevant molecular orbitals for VO_2^- and VO_2 (see Figure 1).

calculated $10a_1$, $11a_1$, and $4b_1$ orbitals for VO_2^- and VO_2 . To obtain a consistent set of orbitals for each charge state, these orbitals are from state-averaged CASSCF calculations. The orbitals by Hendrickx and Tran are optimized for each state, but a meaningful comparison of orbital occupations is facilitated by the use of the same orbitals between different states, as provided in state-averaged calculations. These use the same active space and basis set as those described in our paper, but at a fixed geometry with a VO bond length of 1.62 Å and a OVO bond angle of 110° , rather than the equilibrium anion BPW91 geometry, to better serve as a compromise between the various neutral states. The neutral calculations are state-averaged over the low-lying 2B_1 and two 2A_1 states, while the anion calculations are state-averaged over the nearly degenerate 3B_1 and 3A_1 states. As Figure 2 shows, the $10a_1$ anion and neutral orbitals are very similar to one another, as are the $11a_1$ and $4b_1$ orbitals. Projecting the neutral orbitals to the anion MO basis (Table 1), we can see that although there is mixing of orbital character due to relaxation, the $10a_1$, $11a_1$, and $4b_1$ orbitals are qualitatively similar in anionic and neutral VO_2 .

We next consider the molecular orbital configurations contributing to the various anion and neutral electronic states. The results from our CASSCF calculations are shown in Table 2. Only those contributions with coefficients with absolute

Table 1. Projections of the Relevant State-Averaged Neutral Orbitals in the Basis of the Anion State-Averaged Molecular Orbitals^a

neutral orbital	projection in anion orbital basis
$ 10a_1^{(0)}\rangle$	$0.81 10a_1^{(-)}\rangle + 0.26 11a_1^{(-)}\rangle + 0.44 12a_1^{(-)}\rangle$
$ 11a_1^{(0)}\rangle$	$0.14 10a_1^{(-)}\rangle - 0.95 11a_1^{(-)}\rangle + 0.23 12a_1^{(-)}\rangle$
$ 4b_1^{(0)}\rangle$	$0.99 4b_1^{(-)}\rangle$

^aOnly those with coefficients >0.05 are shown. Orbitals with a (0) superscript correspond to neutral orbitals, while those with a (−) superscript are anion orbitals.

Table 2. Energies (eV) and Leading Configurations of the Low-Lying VO_2 and VO_2^- States by CASSCF

	state	energies	leading configurations
anion	\tilde{A}^3A_1	0.00	$0.91(10a_1)^1(11a_1)^1$
	\tilde{X}^3B_1	0.15	$0.91(10a_1)^1(4b_1)^1$
neutral	\tilde{B}^2A_1	1.04	$0.39(10a_1)^1 + 0.79(11a_1)^1$
	\tilde{A}^2B_1	0.74	$0.90(4b_1)^1$
	\tilde{X}^2A_1	0.00	$-0.77(10a_1)^1 + 0.42(11a_1)^1$

value >0.1 are given. One can see that the relevant anion states are well-approximated by single MO configurations, as is the neutral \tilde{A}^2B_1 state. While the neutral \tilde{X}^2A_1 and \tilde{B}^2A_1 states are mixtures of the $\dots(10a_1)^1$ and $\dots(11a_1)^1$ configurations, the former is clearly the largest contribution to the \tilde{X}^2A_1 state. Hence, removal of an electron from the $4b_1$ orbital of the anion \tilde{X}^3B_1 state to form the neutral \tilde{X}^2A_1 state is a valid one-electron transition. Furthermore, the $\tilde{X}^3B_1 \rightarrow \tilde{B}^2A_1$ transition should have sufficient one-electron character to be observed experimentally, though it is formally a two-electron $(4b_1)^{-1}(10a_1)^1(11a_1)^{-1}$ transition.

In the Hendrickx paper, the dominant MO configurations of the anion \tilde{X}^3B_1 and neutral \tilde{X}^2A_1 states are given as $\dots(10a_1)^0(11a_1)^1(4b_1)^1$ and $\dots(10a_1)^1(11a_1)^0$, respectively, but they label their MO's differently; by appearance, their $10a_1$ MO looks like our $11a_1$ MO and vice versa. Translating their labeling scheme into ours yields $\dots(10a_1)^1(4b_1)^1$ and $\dots(11a_1)^1$ as the dominant configurations for the anion \tilde{X}^3B_1 and neutral \tilde{X}^2A_1 states. These configurations are not connected by a one-electron transition, and this observation was used by Hendrickx and Tran to argue that the X band originates from the \tilde{A}^3A_1 anion state and not the ground state. From Table 2, the anion MO configuration is the same in the two papers, but their MO configuration for the neutral \tilde{X}^2A_1 state differs from ours (and in fact is close to what we find for the neutral \tilde{B}^2A_1 state), although they find it to have largely single-reference character. The origins of these discrepancies are unclear at this time.

Turning now to experimental considerations, we cool the anions to approximately 10 K to minimize contributions in the SEVI spectrum from vibrational hot bands and electronically excited anion states.⁴ The VO_2^- SEVI spectra show no evidence for vibrational hot bands, and since the lowest frequency anion vibrational mode, $\sim 270 \text{ cm}^{-1}$, is comparable to the calculated term energy of the anion \tilde{A}^3A_1 state,⁵ we would expect a negligible contribution to the SEVI spectrum from this state. If one were ignore this point and accept the key results from the Hendrickx paper, namely the presence of both anion states, their MO configurations, and minimal multireference effects, then there would be four fully allowed one-electron transitions within the energy range accessed by the SEVI spectra: the $\tilde{X}^3B_1 \rightarrow \tilde{A}^2B_1$ and $\tilde{X}^3B_1 \rightarrow \tilde{B}^2A_1$ transitions and the two one-electron transitions on the right-hand side of Figure 1. The $\tilde{X}^3B_1 \rightarrow \tilde{B}^2A_1$ and $\tilde{A}^3A_1 \rightarrow \tilde{B}^2A_1$ transitions would be in the vicinity of band B, separated by the anion term energy. However, we observed only one band in this spectral region, and only three bands in total were seen. Finally, our Franck–Condon calculations and those by Hendrickx and Tran disagree slightly on the match of the 3B_1 or 3A_1 states for the originating anion of the X band. Although their calculations were at a more sophisticated CCSD(T) level, the overall differences in the simulations are minor and within the error of even high-level calculations.

Based on the experimental and theoretical considerations outlined here, there is no compelling evidence in favor of the alternative assignment of band X proposed by Hendrickx and Tran nor for any contribution from the anion \tilde{A}^3A_1 state to the SEVI spectrum.

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Notes

The authors declare no competing financial interest.

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