

V₄O₁₀: Spectroscopic Fingerprint of a Well-Defined, Molecular Metaloxo Aggregate[†]

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V₄O₁₀ can be considered as a molecular model for oxovanadium clusters deposited on the surfaces of corresponding heterogeneous catalysts, and here its generation, matrix isolation, and comprehensive characterization by IR, Raman, and UV/vis spectroscopy are described.

Supported vanadium oxides represent an important class of heterogeneous catalysts for hydrocarbon oxidation because they lead to high selectivities and turnover rates for many processes.¹ Typically, the nature of the active surface of such catalysts varies rather strongly, and single-site, di- and polynuclear species, vanadium oxo clusters as well as monolayers are postulated according to the results of spectroscopic analyses.²

However, the unambiguous identification of the real surface structure remains difficult because (i) several different active species can exist in parallel, (ii) the employed analytic and spectroscopic methods (e.g., IR, Raman, and UV/vis) usually average over all existing species present, and (iii) the spectroscopic signatures of the different surface species are still discussed controversially.³

Therefore, the characterization of unligated vanadium oxo clusters as well-defined reference systems and the investigation of their reactivity^{4a–h} are very meaningful. This is emphasized, for example, by the results of work on deposited vanadium oxide particles as catalyst model systems in which V₄O₁₀ aggregates play a central role.⁵ In this context, the gas-phase IR spectrum of the radical anion V₄O₁₀⁻⁴ⁱ and reactivity studies on the radical cation V₄O₁₀^{+4j,k} were reported recently. Not surprisingly, these species are highly

reactive toward organic substrates because of their open shell, which, however, at the same time confines their potential as models.

This contribution deals with the *neutral* particle V₄O₁₀. The results of mass spectrometric investigations quite early led to the suggestion that the vapor phase above heated vanadium(V) oxide mainly contains V₄O₁₀ molecules for which a cage structure with tetrahedral symmetry analogous to that of P₄O₁₀ was proposed (see inset in Figure 1).⁶ This was the first hint to this molecule, and it initiated preliminary matrix isolation studies by Beattie et al., during the course of which the gas evaporating from a Knudsen cell with V₂O₅ heated to 700–900 °C was isolated in a nitrogen matrix. The IR spectrum of this matrix showed two bands that were assigned to V₄O₁₀, because the band pattern obtained after isotope enrichment resembled the one that had been observed previously for P₄O₁₀ and As₄O₆, respectively.⁷ However, only low concentrations were achieved within such matrices and, hence, only the most intensive IR absorptions of V₄O₁₀ were identified as clear signals. This might be due to the fact that V₂O₅ continuously decomposes upon heating via reductive

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- (1) van Santen, R. A.; Neurock, M. *Molecular Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2006.
- (2) (a) Weckhuysen, B. M.; Keller, D. E. *Catal. Today* **2003**, *78*, 25–46. (b) Wachs, I. E. *Catal. Today* **2005**, *100*, 79–94.
- (3) Magg, N.; Immaraporn, B.; Giorgi, J. B.; Schroeder, T.; Bäumer, M.; Döbler, J.; Wu, Z.; Kondratenko, E.; Cherian, M.; Baerns, M.; Stair, P. C.; Sauer, J.; Freund, H.-J. *J. Catal.* **2004**, *226*, 88–100.

- (4) (a) Bell, R. C.; Castleman, A. W. *J. Phys. Chem. A* **2002**, *106*, 9893. (b) Feyel, S.; Schwarz, H.; Schröder, D.; Daniel, C.; Hartl, H.; Döbler, J.; Sauer, J.; Santambrogio, G.; Wöste, L.; Asmis, K. *ChemPhysChem* **2007**, *8*, 1640. (c) Zemski, K. A.; Justes, D. R.; Castleman, A. W. *J. Phys. Chem. A* **2001**, *105*, 10237. (d) Fiellicke, A.; Rademann, K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2621–2628. (e) Zemski, K. A.; Justes, D. R.; Mitrić, R.; Moore, N. A.; Bonačić-Koutecký, V.; Castleman, A. W. *J. Am. Chem. Soc.* **2003**, *125*, 6289–6299. (f) Justes, D. R.; Moore, N. A.; Castleman, A. W. *J. Phys. Chem. B* **2004**, *108*, 3855. (g) Feyel, S.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2006**, *110*, 2647–2654. (h) Feyel, S.; Schröder, D.; Rozanska, X.; Sauer, J.; Schwarz, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 4677–4681. (i) Asmis, K. R.; Santambrogio, G.; Brümmer, M.; Sauer, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3122–3125. (j) Asmis, K. R.; Brümmer, M.; Kaposta, C.; Santambrogio, G.; von Helden, G.; Meijer, G.; Rademann, K.; Wöste, L. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1101–1104. (k) Feyel, S.; Döbler, J.; Schröder, D.; Sauer, J.; Schwarz, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 4681–4685.
- (5) Guimond, S.; Abu Haija, M.; Kaya, S.; Lu, J.; Weissenrieder, J.; Shaikhutdinov, S.; Kühlenbeck, H.; Freund, H.-J.; Döbler, J.; Sauer, J. *Top. Catal.* **2006**, *38*, 117–125.
- (6) (a) Berkowitz, J.; Chupka, W. A.; Inghram, M. G. *J. Chem. Phys.* **1957**, *27*, 87–90. (b) Farber, M.; Uy, O. M.; Srivastava, R. D. *J. Chem. Phys.* **1972**, *56*, 5312–5315.
- (7) Beattie, I. R.; Ogden, J. S.; Price, D. D. *Inorg. Chem.* **1978**, *17*, 3296.
- (8) Vyboishchikov, S. F.; Sauer, J. *J. Phys. Chem. A* **2001**, *105*, 8588.

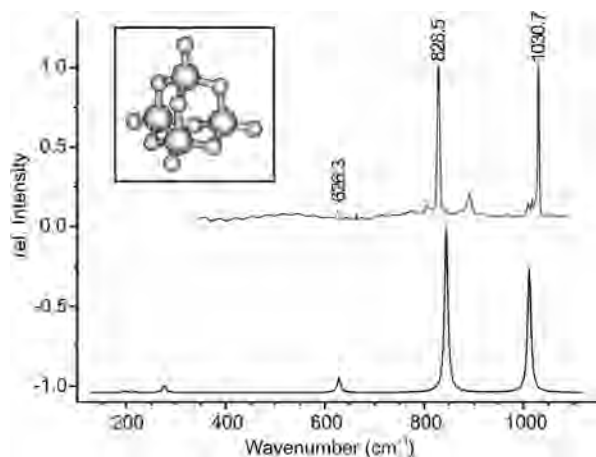


Figure 1. IR spectrum of V_4O_{10} . Top trace: measured (N_2 matrix, $T = 10$ K). Bottom trace: calculated (B3LYP/TZVP). Inset: calculated structure of V_4O_{10} .⁸

Table 1. IR Absorptions of V_4O_{10} (in cm^{-1}) in Low-Temperature matrices (Only the Bands belonging to the Most Favourable Matrix Sites Are Listed)

N_2 matrix (lit. ⁷)	N_2 matrix	Ar matrix
1029.9	1030.7	1028.4
828.4	828.5	826.8
~626 ^a	626.3	~623

^a Weak absorption, in lit.⁷ tentatively assigned.

elimination of O_2 under the formation of low-valent oxo compounds, which are more difficult to vaporize.

For a more comprehensive characterization of V_4O_{10} and the reproducible generation of matrices with high V_4O_{10} content for reactivity studies, we employed a newly built high-vacuum furnace. Crucial for the success of the experiments were the construction of a vaporization cell where a constant flow of liquid V_2O_5 moistens the exit channel of the cell during operation and the careful choice of a temperature program that keeps the balance between a low decomposition rate of the vanadium oxide, on the one hand, and a high deposition rate, on the other hand. Simultaneous deposition of V_4O_{10} effusing from the vaporization cell and dinitrogen onto a cooled CsI substrate ($T = 10$ K) under high vacuum resulted in a matrix whose IR spectrum is shown in Figure 1. In contrast to the work of Beattie et al., not only the already known IR absorptions at 1030.7 and 828.5 cm^{-1} but also the weak band of the V–O–V bending vibration at 626.3 cm^{-1} are now identifiable as clear signals. Moreover, in high-resolution IR spectra (resolution 0.25 cm^{-1} instead of 1 cm^{-1}), it appeared that the V_4O_{10} signals consist actually of several superimposed bands. These belong most likely to V_4O_{10} molecules occupying different sites within the matrix packing. The band splitting caused thereby (“matrix splitting”) is larger for argon as the host matrix than for nitrogen (for details, see the Supporting Information). Annealing of the matrices causes the growth of the IR bands belonging to the most favorable positions (Table 1) at the expense of the others.

Further weak bands that can be recognized in the IR spectrum indicate the presence of two other vanadium oxide species in low concentrations. According to the mentioned

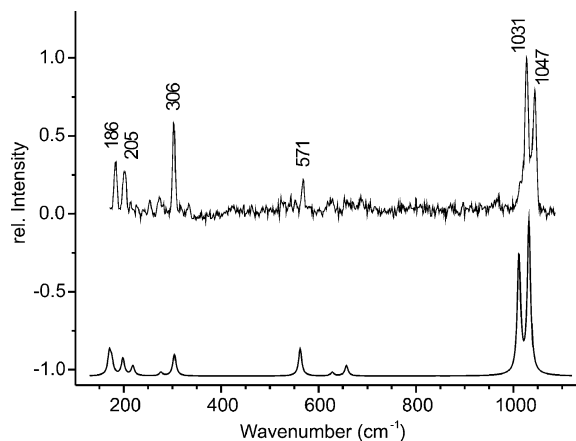


Figure 2. Raman spectrum of V_4O_{10} . Top trace: measured (N_2 matrix, $T = 10$ K, laser: $\lambda = 514.5$ nm, $P = 250$ mW). Bottom trace: calculated (B3LYP/TZVP).

mass spectrometric investigations,⁶ small amounts of V_4O_8 and even less V_6O_{14} , V_6O_{12} , and V_2O_4 can be generated besides V_4O_{10} upon heating of V_2O_5 . Hence, the double band at 1010/1017 cm^{-1} is assigned to V_4O_8 (in agreement with the IR spectrum calculated for this molecule; see the Supporting Information), and the band at 891 cm^{-1} is assigned to the species V_6O_{14} and V_6O_{12} (by analogy to the IR spectrum calculated⁸ for V_6O_{15} and bearing in mind the mass spectrometric results).

To go further into the characterization of V_4O_{10} , the application of Raman and UV/vis spectroscopy, i.e., standard methods for the investigation of surface species belonging to supported vanadium oxide catalysts, was pursued also. While for the characterization of low-temperature matrices UV/vis spectroscopy represents a common method, recording Raman spectra is an experimental challenge because of the possible matrix destruction by laser light and the low substrate concentrations in combination with the relatively low intensity of the Raman scattering. However, especially for a highly symmetric molecule like V_4O_{10} , quite a number of Raman-active oscillations are to be expected and thus it seemed worthwhile to attempt the determination of the Raman spectrum. For this purpose, a vacuum chamber for the cold matrix head was developed, which allows examination of one and the same matrix with IR, Raman, and UV/vis spectroscopy.

The Raman spectrum of V_4O_{10} is shown in Figure 2, where it is confronted (as the IR spectrum in Figure 1) with a calculated spectrum obtained on a theoretical level (B3LYP/TZVP),⁹ which is comparable with that of the former work on the structure and the IR frequencies of V_4O_{10} .⁸ The agreement of the experimentally obtained spectra with the theoretically predicted signal patterns is obvious. According to the calculations, the only band with a high intensity in both the IR and Raman spectra (1031 cm^{-1}) belongs to out-of-phase oscillations of the four terminal V=O groups. The totally symmetrical oscillation with the V=O groups all moving in phase can be observed in the Raman spectrum at 1047 cm^{-1} . The bands with lower wavenumbers belong to

(9) Frisch, M. J.; et al. *Gaussian 03*; see the Supporting Information.

oscillations corresponding mainly to movements of the V–O–V framework.

Generally, by rotation of the polarization plane of the stimulating laser light, the depolarization ratios ρ of Raman bands can be estimated. This allows for the assignment of the Raman bands to totally symmetrical ($0 \leq \rho < 0.75$) and not totally symmetrical ($\rho = 0.75$) molecular vibrations. According to the calculations for V_4O_{10} , the experimental bands at 1047, 571, and 306 cm^{-1} should correspond to totally symmetrical vibrations. This is in qualitative agreement with the fact that we have found for these three bands considerably lower depolarization ratios than those for the remaining bands.

In addition, the Raman spectroscopic investigations showed that besides V_4O_{10} the matrices also contained O_2 (band at 1555 cm^{-1}), a product of the partial thermal decomposition of V_2O_5 in the furnace (see above). This information, which naturally cannot be obtained with IR spectroscopy, is highly relevant for the realization of reactivity studies in the future.

As a third method, UV/vis spectroscopy was applied to the matrix-isolated V_4O_{10} molecules in order to obtain information about typical absorptions, which can be valuable in many ways. In the course of the characterization of vanadium oxide catalysts, it has been found that the activity of supported vanadium oxide catalysts correlates with the UV/vis absorption edge,¹⁰ and furthermore it turned out that they usually possess significantly greater band gaps than the corresponding bulk material,^{10,11} which is not understood. This has led Wang et al. to perform a photoelectron spectroscopic (PES) investigation of $V_4O_{10}^-$ anions in the gas phase,¹² which allowed to infer an experimental measure of the HOMO–LUMO gap for the neutral cluster, although strictly speaking this represents the singlet–triplet excitation in V_4O_{10} . A HOMO–LUMO gap of 2.58 eV was derived that is significantly higher than the one of bulk V_2O_5 . Hence, it was suggested that the enlarged HOMO–LUMO gaps in such clusters may be related to the observations made for the supported vanadia catalysts, implying that highly stable cage species may be present on oxidic surfaces and play a role in catalysis.¹²

Naturally, PES allows only indirect conclusions on intramolecular electron-transfer processes. The UV/vis spectrum of V_4O_{10} , reflecting directly the dipole-allowed (vertical) electronic transitions, is shown in Figure 3.

V_4O_{10} matrices are colorless, and hence it is not a surprise that in the visible region no absorption bands are observed;

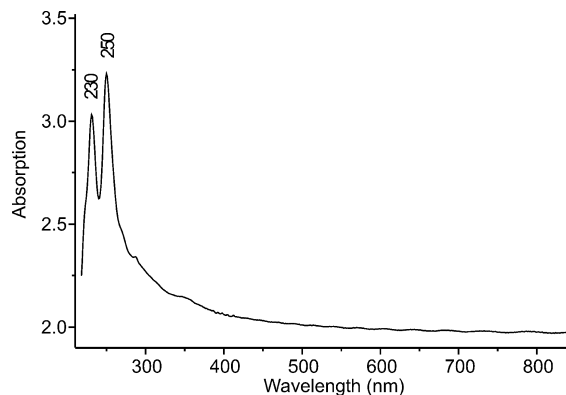


Figure 3. UV/vis spectrum of V_4O_{10} (N_2 matrix, $T = 10$ K).

however, two distinct bands appear in the UV area (at 250 and 230 nm). The energies of 5.0 and 5.4 eV corresponding to these wavelengths are considerably higher than the HOMO–LUMO gap found by Wang et al.¹² This discrepancy may be attributed to the fact that, first, singlet–triplet transitions (vide supra) are optically forbidden and usually cannot be seen in UV/vis spectra. Second, for allowed singlet–singlet transitions, the intensities are determined by the corresponding transition dipole moments. It can be expected that there are further allowed singlet–singlet transitions of much lower energies than the observed ones,¹² which, however, have just small transition dipole moments and hence do not contribute to the UV/vis spectrum significantly. For inferences concerning the surfaces of supported vanadia catalysts, it is thus helpful to now also have information concerning the UV/vis spectrum of V_4O_{10} available, in addition to the valuable data derived by Wang et al.

In summary, with V_4O_{10} , an unsupported, well-defined, neutral vanadium oxo species containing only a few atoms was investigated, which is of considerable importance as a reference system for investigations concerning real catalysts and for the interpretation of the various results obtained for deposited vanadium oxide particles. Future research will now fathom its potential to also act as a functional model that can reveal information concerning elementary reaction steps during processes catalyzed by vanadia-based materials.

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Supporting Information Available: Experimental and computational details, IR absorptions of V_4O_{10} at minor matrix sites, and calculated vibrational spectra of V_4O_{10} and V_4O_8 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) (a) Khodakov, A.; Olthof, B.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, *181*, 205. (b) Chen, K. D.; Bell, A. T.; Iglesia, E. *J. Catal.* **2002**, *209*, 35. (c) Gao, X.; Wachs, I. E. *J. Phys. Chem. B* **2000**, *104*, 1261. (d) Gao, X.; Wachs, I. E.; Wong, M. S.; Ying, J. Y. *J. Catal.* **2001**, *203*, 18.
- (11) (a) Wachs, I. E.; Chen, Y.; Jehng, J. M.; Briand, L. E.; Tanaka, T. *Catal. Today* **2003**, *78*, 13. (b) Wachs, I. E.; Briand, L. E.; Jehng, J. M.; Burcham, L.; Gao, X. *Catal. Today* **2000**, *57*, 323.
- (12) Zhai, H.-J.; Döbler, J.; Sauer, J.; Wang, L.-S. *J. Am. Chem. Soc.* **2007**, *129*, 13270–13276.