

Experimental Identification of the Active Site in the Heteronuclear Redox Couples $[AlVO_x]^{+•}/CO/N_2O$ ($x = 3, 4$) by Gas-Phase IR Spectroscopy

Sreekanta Debnath, Harald Knorke, Wieland Schöllkopf, Shaodong Zhou,* Knut R. Asmis,* and Helmut Schwarz*

Dedicated to Professor Hans-Joachim Freund and Professor Joachim Sauer

Abstract: Cryogenic ion vibrational spectroscopy was used in combination with electronic structure calculations to identify the active site in the oxygen atom transfer reaction $[AlVO_4]^{+•} + CO \rightarrow [AlVO_3]^{+•} + CO_2$. Infrared photodissociation spectra of messenger-tagged heteronuclear clusters demonstrate that in contrast to $[AlVO_4]^{+•}$, $[AlVO_3]^{+•}$ is devoid of a terminal $Al-O_t$ unit while the terminal $V=O_t$ group remains intact. Thus it is the $Al-O_t$ moiety that forms the active site in the $[AlVO_x]^{+•}/CO/N_2O$ ($x = 3, 4$) redox couples, which is in line with theoretical predictions.

Arguably, the metal-mediated conversion of CO into CO_2 constitutes one of the best-studied oxidation processes, both at surfaces^[1] and in the gas phase.^[2] Catalytic conversions of harmful gases that are produced in fossil-fuel combustions, such as CO or the oxides of nitrogen, into N_2 and CO_2 are of particular importance, both environmentally as well as economically. While these redox reactions are quite exothermic, for example, $\Delta_r H = -365 \text{ kJ mol}^{-1}$ for the reaction $N_2O + CO \rightarrow N_2 + CO_2$, they do not occur directly to any measurable extent at either room or elevated temperature. This impediment is due to the high activation barriers, which exceed 197 kJ mol^{-1} for the N_2O/CO system. Catalysts are

required to bypass the barrier by opening up new, energetically less demanding pathways. The combination of computational studies with gas-phase experiments has proven helpful in this endeavor, shedding new light on the catalytic mechanisms that operate at a strictly atomistic level.^[2] For example, in a landmark experiment, Kappes and Staley^[3] demonstrated that a single Fe^+ atom can superbly mediate the coupled redox processes described in Equations (1) and



(2) under ambient conditions. Theoretical work, comple-



mented by experimental studies over an extended temperature regime, revealed fascinating details concerning the electronic structure requirements and dynamic aspects of oxygen atom transfers (OATs) in this system,^[4] which involve a two-state reactivity scenario.^[5]

Subsequently, numerous other atomic main-group and transition-metal cations have been tested, mostly by the Böhme group^[6] and others.^[2g,7] More recently, the focus of activity has shifted to the investigation of metal oxide clusters, in particular heteronuclear ones, to uncover the underlying mechanisms.^[2f,g] Here, one of the pertinent challenges concerns the identification of the active site^[8] in the metal oxide cluster, the so-called aristocratic atom.^[9]

The redox couple $[AlVO_x]^{+•}/CO/N_2O$ ($x = 3, 4$) may serve as a good example.^[10] At room temperature and under single-collision conditions, the heteronuclear oxide cluster $[AlVO_4]^{+•}$ is reduced to $[AlVO_3]^{+•}$ in the presence of CO, and if N_2O is added, re-oxidation occurs. Both OATs proceeded cleanly and with reaction efficiencies of 59% and 65%, relative to the collision rate, respectively. In principle, the turnover number (TON) of this ideal catalytic cycle (Scheme 1) is infinite; however, in reality, the TON is limited by side reactions with background impurities, for example, hydrogen atom abstraction from hydrocarbons.^[10]

DFT calculations have provided insight into parts of the mechanism responsible for these redox processes. Furthermore, theory predicted that in the course of the OAT (Scheme 1), the active site should involve exclusively the terminal $Al-O_t$ unit of $[AlVO_4]^{+•}$. In contrast, the $V=O_t$ moiety of $[AlVO_4]^{+•}$ cannot provide an oxygen atom in the

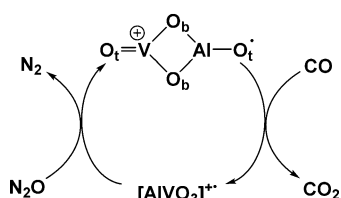
[*] Prof. Dr. S. Zhou, Prof. Dr. H. Schwarz

Institut für Chemie
Technische Universität Berlin
Straße des 17. Juni 135, 10623 Berlin (Germany)
E-mail: Helmut.Schwarz@tu-berlin.de

Prof. Dr. S. Zhou
Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering
Manufacture Technology
College of Chemical and Biological Engineering
Zhejiang University
310027 Hangzhou (P. R. China)
E-mail: szhou@zju.edu.cn

M. Sc. S. Debnath, Dipl.-Phys. H. Knorke, Prof. Dr. K. R. Asmis
Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie
Universität Leipzig
Linnéstr. 2, 04103 Leipzig (Germany)
E-mail: knut.asmis@uni-leipzig.de

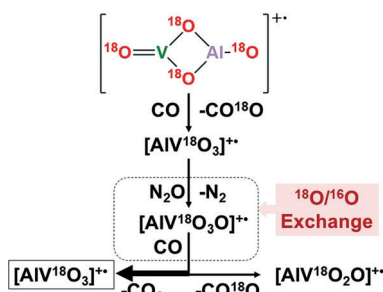
M. Sc. S. Debnath, Dr. W. Schöllkopf
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, 14195 Berlin (Germany)



Scheme 1. Oxygen atom transfer in the redox couple $[\text{AlVO}_4]^+/\text{CO}/\text{N}_2\text{O}$.

oxidation of CO on both kinetic and thermodynamic grounds.^[10]

By definition, the active site of the cluster cannot be identified in a labeling experiment with, for example, $[\text{AlV}^{18}\text{O}_4]^+/\text{CO}/\text{N}_2\text{O}$. Nevertheless, inspection of the branching ratio for the final product pairs $\text{CO}_2/[\text{AlV}^{18}\text{O}_3]^+$ versus $\text{C}^{18}\text{OO}/[\text{AlV}^{18}\text{O}_2\text{O}]^+$ reveals some interesting details (Scheme 2). The first step, that is, the reduction of



Scheme 2. ^{18}O labeling experiments.

$[\text{AlV}^{18}\text{O}_4]^+$ to $[\text{AlV}^{18}\text{O}_3]^+$ by CO, occurs without any measurable $^{18}\text{O}/^{16}\text{O}$ exchange, and the trioxide is cleanly generated. Similarly, re-oxidation of the latter with N_2O gives rise to $[\text{AlV}^{18}\text{O}_3\text{O}]^+$ exclusively. Based on CCSD(T, full)/CBS//B3LYP-D3(BJ)/cc-pVTZ calculations, this re-oxidation step of the cluster is extremely exothermic (-219 kJ mol^{-1}); thus, while part of the liberated energy is carried off as kinetic energy, the product ion generated is rovibrationally quite hot, and in the absence of (or prior to) efficient collisional cooling, it may undergo degenerate intramolecular isomerization processes in the course of which the $\text{Al}-\text{O}_t$ unit is converted to some extent into an $\text{Al}-^{18}\text{O}_t$ group.^[11] Consequently, in the final reaction of $[\text{AlV}^{18}\text{O}_3\text{O}]^+$ with CO, both unlabeled and labeled carbon dioxide molecules are liberated with a branching ratio of approximately 2.8:1. Variation of the delay time between the individual reaction steps or changing the thermalization conditions, which is limited in our experimental FT-ICR set-up, did not bring about any substantial changes in this branching ratio. Therefore, the question then still remains open as to which of the two terminal MO bonds ($M = \text{V}, \text{Al}$) of the metal oxide cluster is involved in the redox process.

Herein, we verify this theoretical prediction^[10] by recording gas-phase infrared photodissociation (IRPD) spectra of messenger-tagged $[\text{AlVO}_x]^+$ ($x = 3, 4$) using the intense and widely tunable radiation from an IR free electron laser

(FEL)^[12] and comparing them with simulated IR spectra of various isomers.^[13] The result is unambiguous and confirms the theoretical analysis.

Figure 1 shows the computed harmonic IR spectra of four stable $[\text{AlVO}_4]^+$ isomers (**1–4**) as well as that of isomer **1** “tagged” with He as a messenger atom (**1•He**; for technical details and references, see the Supporting Information). The global ground state of $[\text{AlVO}_4]^+$ is a doublet electronic state. Its structure is characterized by a four-membered $\text{V}(\mu\text{-O})_2\text{-Al}$ ring containing terminal VO and AlO units (Figure 1, **1**); similar bonding patterns have previously been reported for $[\text{Zr}_2\text{O}_4]^+$,^[14] $[\text{V}_2\text{O}_4]^+$,^[15] $[\text{CeVO}_4]^+$,^[16] $[\text{VPO}_4]^+$,^[17] $[\text{Al}_2\text{O}_4]^-$,^[18] and $[\text{Ti}_2\text{O}_4]^-$.^[19] The other isomers considered were predicted to be $> 100 \text{ kJ mol}^{-1}$ higher in energy, ruling them out as possible candidates purely on energetic grounds. These isomers include the chain-like structure **4** (121 kJ mol^{-1}) and the two cyclic variants containing a terminal $\text{Al}(\text{O}_2)$ group (**2**; 140 kJ mol^{-1}) and a terminal VO_2 unit (**3**;

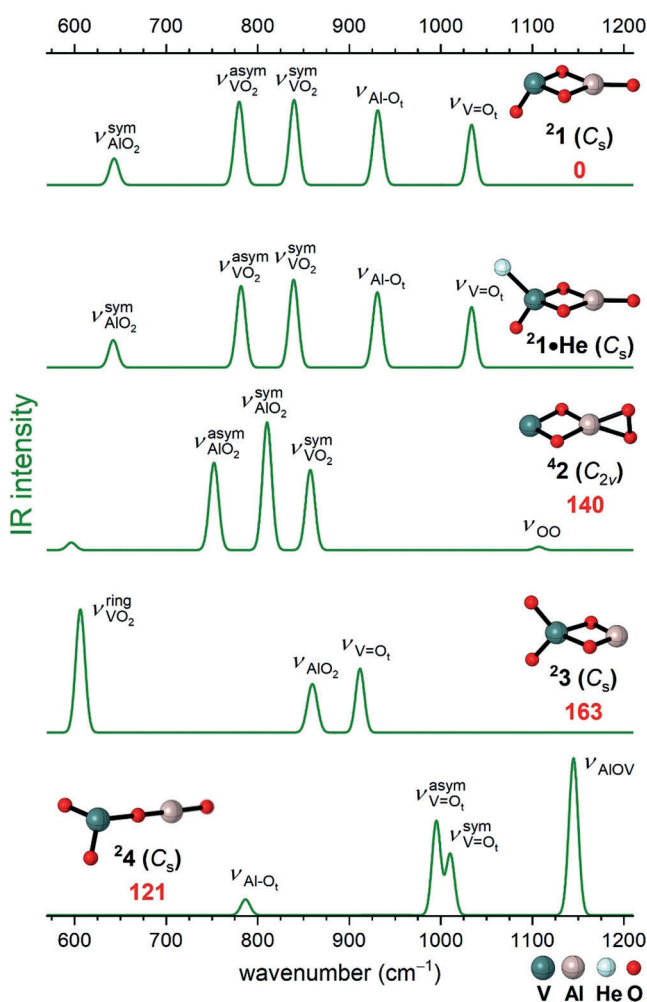


Figure 1. Simulated IR spectra of **21**, **21•He**, **42**, **23**, and **24** as calculated at the B3LYP-D3(BJ)/cc-pVTZ level of theory. The numbers in red give the relative energies (in kJ mol^{-1}) of different isomers of the $[\text{AlVO}_4]^+$ species as calculated at the CCSD(T,full)/CBS(cc-pVD:TZ)//B3LYP-D3(BJ)/cc-pVTZ level of theory. Harmonic frequencies of the $\text{V}=\text{O}$ modes are scaled by 0.9167, and all other modes by 0.9832. For further details, see Table 1 as well as Table S1 and Figure S1.

163 kJ mol⁻¹). Note that tagging cluster **1** with a helium atom does not perturb the IR spectrum significantly.

A comparison of the computed IR spectra of the [AlVO₄]⁺ isomers **1** to **4** (Figure 1) with the experimental IRPD spectrum of He-tagged [AlVO₄]⁺ (panel I in Figure 2) leaves no doubt that the global-minimum-energy structure **1** is formed exclusively upon laser ablation (see the Supporting Information, Figure S2) and subsequent helium tagging in the cold ion trap. Comparing the relevant frequencies

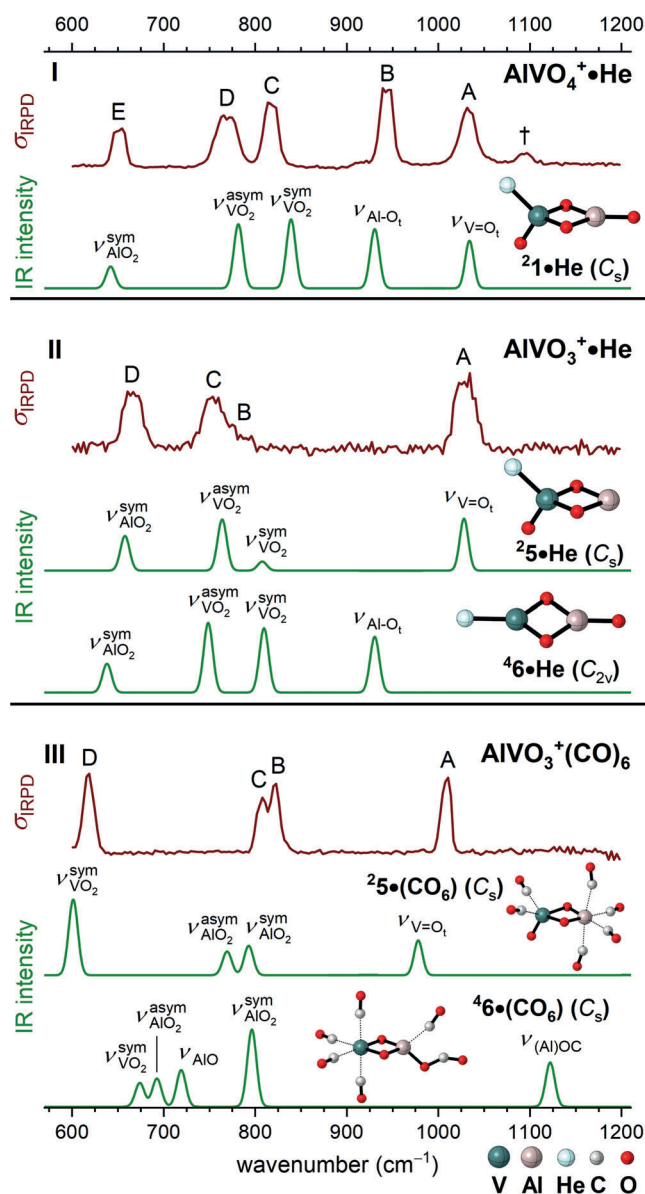


Figure 2. The experimental IRPD spectra (dark red) and the harmonic IR spectra (green) of I) [AlVO₄]⁺•He, II) [AlVO₃]⁺•He, and III) [AlVO₃]⁺(CO)₆. The messenger-tagged clusters were produced either by mass-selecting the corresponding bare cations and subsequently tagging them with He in the ion trap at 12 K (I and II) or by trapping [AlVO₄]⁺ in a CO/He gas mixture at 60 K (III). The simulated IR spectra were determined from scaled B3LYP-D3(BJ)/cc-pVTZ harmonic frequencies and intensities and convoluted with a 10 cm⁻¹ full width at half maximum (FWHM) Gaussian line shape function. See Table 1 for the band positions and assignments.

(Table 1) shows satisfying to excellent agreement given the limitations of the harmonic approximation used in the simulation.

Table 1: Experimental band labels and positions, scaled harmonic B3LYP-D3(BJ)/cc-pVTZ vibrational wavenumbers, and band assignments. Values in parentheses indicate the FWHM of the observed bands.

System/band	Experiment [cm ⁻¹]	Scaled harmonic wavenumber [cm ⁻¹]	Assignment
[AlVO₄He]⁺			
†	1094 (17)	n.a.	overtone antisymmetric AlO ₂ stretch
A	1032 (19)	1034 ^[a]	VO stretch
B	943 (16)	930 ^[b]	AlO stretch
C	817 (18)	839 ^[b]	symmetric VO ₂ stretch
D	769 (28)	781 ^[b]	antisymmetric VO ₂ stretch
E	651 (16)	641 ^[b]	symmetric AlO ₂ stretch
[AlVO₃He]⁺			
A	1029 (21)	1028 ^[a]	VO stretch
B	783 (20)	808 ^[b]	symmetric VO ₂ stretch
C	754 (24)	764 ^[b]	antisymmetric VO ₂ stretch
D	666 (20)	658 ^[b]	symmetric AlO ₂ stretch
[AlVO₃(CO)₆]⁺			
A	1008 (10)	978 ^[a]	VO stretch
B	822 (10)	793 ^[b]	symmetric AlO ₂ stretch
C	807 (11)	769 ^[b]	antisymmetric AlO ₂ stretch
D	618 (12)	601 ^[b]	symmetric VO ₂ stretch

[a] Scaling factor: 0.9167 (VO stretches). [b] Scaling factor: 0.9832 (all other modes).

The three intense IRPD bands A–C proved to be particularly diagnostic for the discussion from which site of the heteronuclear cluster [AlVO₄]⁺ the oxygen atom is abstracted in the reduction. Band A at 1032 cm⁻¹ was assigned to the terminal V=O_t stretching mode of **1**, which is in line with the IRPD data reported previously for [V₂O₄]⁺ and [VPO₄]⁺. Bands B (943 cm⁻¹) and C (817 cm⁻¹) correspond to the stretching of the terminal Al–O_t group and the symmetric OVO ring stretching mode, respectively.

When [AlVO₃]⁺ was generated directly by laser ablation (Figure S2) and subsequently tagged with He, its IRPD spectrum (spectrum II in Figure 2) was in excellent agreement with the one simulated for **5**•He, confirming that also in this case, the global-minimum-energy isomer is formed exclusively. This species is devoid of an Al–O_t unit but contains a V=O_t bond. In contrast, isomer **6**, in which the Al–O_t unit is preserved, is 106 kJ mol⁻¹ higher in energy than **5**, and, more importantly, the predicted IR spectrum of **6**•He does not match the experimental one (Figure 2).

Before moving on, a brief comment on the origin of the weaker IR band B (783 cm⁻¹) in panel II, which was assigned to the symmetric OVO ring stretching mode, might be helpful. This mode gives rise to the strong absorption band C in [AlVO₄]⁺•He (panel I), and the substantial drop in intensity is

due to the rather small change in the dipole moments associated with this vibration for the $[\text{AlVO}_3]^{+\bullet}$ cluster (for details, see Figure S1).

Next, we will address the central question as to whether isomer **5** is also and solely generated from the redox couple $[\text{AlVO}_4]^{+\bullet}/\text{CO}$. This experiment was performed with CO seeded in He gas at slightly higher temperatures (60 K) to avoid CO condensation on the ion trap walls. The obtained time-of-flight mass spectrum (see Figure S3) shows that also under multiple collision conditions, $[\text{AlVO}_4]^{+\bullet}$ is very efficiently (> 98%, see Figure S3) converted into $[\text{AlVO}_3]^{+\bullet}$. Additional collisions with CO molecules cannot be avoided under the present conditions, but exclusively lead to “solvated” $[\text{AlVO}_3]^{+\bullet}$ clusters of the type $[\text{AlVO}_3]^{+\bullet}(\text{CO})_{0-7}$, of which the $[\text{AlVO}_3]^{+\bullet}(\text{CO})_6$ complex is formed predominantly (Figure S2). Its IRPD spectrum, obtained by monitoring the CO loss channels, is shown in Figure 2 (panel III). Comparison with the simulated IR spectra of isomers **5**·(CO)₆ and **6**·(CO)₆ clearly demonstrates that it is indeed the main-group aluminum oxide that delivers its oxygen atom in the redox process.^[20] This observation, namely that main-group oxides rather than transition-metal oxides serve as the active site in various catalytic transformations, seems to be a rather general structural feature of quite a few metal oxide clusters;^[21] moreover, as shown in a different context, these centers also play a decisive role in the thermal activation of strong C–H bonds by metal-attached oxyl groups.^[22]

In summary, we have used IRPD spectroscopy to unambiguously identify the active site of the heterogeneous metal oxide cluster $[\text{AlVO}_4]^{+\bullet}$, which serves as a computationally tractable gas-phase model system for studying OAT reactions as part of more complex catalytic cycles.^[23] The strategy employed here, which is based on using highly sensitive mass spectrometry for screening potentially interesting reactions and then applying the more complex methodology of cryogenic ion vibrational spectroscopy, in combination with electronic structure calculations, to resolve structural issues involving isobaric and isomeric species, is generally applicable and will prove helpful in future experiments, for example, in the context of coupling methane with carbon dioxide in the presence of metal-based heterogeneous catalysis.^[24]

Acknowledgements

Generous financial support of the work at TU Berlin by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (“UniCat”) is appreciated. The research of the Asmis group was funded by the Deutsche Forschungsgemeinschaft within the Collaborative Research Center 1109, “Metal Oxide/Water Systems”. The work at Zhejiang University has been supported by the Fundamental Research Funds for the Central Universities of China (2018QNA4040). We thank Dr. Thomas Weiske, Dr. Maria Schlangen-Ahl, Dr. Xiaoyan Sun, and Sandy Gewinner for technical and computational assistance and Andrea Beck for her support in the preparation of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Keywords: active-site characterization · heteronuclear cluster oxides · infrared photodissociation spectroscopy · redox catalysis

- [1] a) H.-J. Freund, G. Meijer, M. Scheffler, R. Schlögl, M. Wolf, *Angew. Chem. Int. Ed.* **2011**, *50*, 10064–10094; *Angew. Chem.* **2011**, *123*, 10242–10275; b) B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **2011**, *3*, 634–641; c) A. Nilsson, J. LaRue, H. Öberg, H. Ogasawara, M. Dell’Angela, M. Beye, H. Öström, J. Gladh, J. K. Nørskov, W. Wurt, F. Abild-Pedersen, L.-G. M. Pettersson, *Chem. Phys. Lett.* **2017**, *675*, 145–173.
- [2] For a selected reviews, see: a) D. K. Böhme, H. Schwarz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2336–2354; *Angew. Chem.* **2005**, *117*, 2388–2406; b) M. L. Kimble, A. W. Castleman, C. Bürgel, V. Bonačić-Koutecký, *Int. J. Mass Spectrom.* **2006**, *254*, 163–167; c) Z.-C. Wang, S. Yin, E. R. Bernstein, *J. Phys. Chem. Lett.* **2012**, *3*, 2415–2419; d) Q.-Y. Liu, S.-G. He, *Chem. J. Chin. Univ.* **2014**, *35*, 665–688; e) S. M. Lang, I. Fleischer, T. M. Bernhardt, R. N. Barnett, U. Landman, *ACS Catal.* **2015**, *5*, 2275–2289; f) H. Schwarz, *Catal. Sci. Technol.* **2017**, *7*, 4302–4314; g) see also the many references in: L.-N. Wang, X.-N. Li, L.-X. Jiang, B. Yang, Q.-Y. Liu, H.-G. Xu, W.-J. Zheng, S.-G. He, *Angew. Chem. Int. Ed.* **2018**, *57*, 3349–3353; *Angew. Chem.* **2018**, *130*, 3407–3411.
- [3] M. M. Kappes, R. H. Staley, *J. Am. Chem. Soc.* **1981**, *103*, 1286–1287.
- [4] a) J. J. Melko, S. G. Ard, J. A. Fournier, J. Li, N. S. Shuman, H. Guo, J. Troe, A. A. Viggiano, *Phys. Chem. Chem. Phys.* **2013**, *15*, 11257–11267; b) V. G. Ushakov, J. Troe, R. S. Johnson, H. Guo, S. G. Ard, J. J. Melko, N. S. Shuman, A. A. Viggiano, *Phys. Chem. Chem. Phys.* **2015**, *17*, 19700–19708.
- [5] a) H. Schwarz, *Int. J. Mass Spectrom.* **2004**, *237*, 75–105; b) D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139–145; c) J. N. Harvey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 331–343; d) S. Shaik, *Int. J. Mass Spectrom.* **2013**, *354/355*, 5–14; e) J. N. Harvey, *WIREs Comput. Mol. Sci.* **2014**, *4*, 1–14.
- [6] a) G. K. Koyanagi, D. K. Böhme, *J. Phys. Chem. A* **2001**, *105*, 8964–8968; b) V. V. Lavrov, V. Blagojevic, G. K. Koyanagi, G. Orlova, D. K. Böhme, *J. Phys. Chem. A* **2004**, *108*, 5610–5624; c) V. Blagojevic, G. Orlova, D. K. Böhme, *J. Am. Chem. Soc.* **2005**, *127*, 3545–3555.
- [7] M. Brönstrup, D. Schröder, I. Kretschmar, H. Schwarz, J. N. Harvey, *J. Am. Chem. Soc.* **2001**, *123*, 142–147.
- [8] J. Sauer, H.-J. Freund, *Catal. Lett.* **2015**, *145*, 109–125.
- [9] H. S. Taylor, *J. Phys. Chem.* **1926**, *30*, 145–171.
- [10] Z.-C. Wang, N. Dietl, R. Kretschmer, T. Weiske, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2011**, *50*, 12351–12354; *Angew. Chem.* **2011**, *123*, 12559–12562.
- [11] A reviewer has surmised that in the oxidation of $^2[\text{AlVO}_3]^{+\bullet}$ with N_2O , electronically excited $^4[\text{AlVO}_4]^{+\bullet}$ may have been co-generated. While this process is spin-forbidden and part of the liberated 219 kJ mol^{-1} energy is carried away as kinetic energy, from an energetic point of view, this possibility cannot be ruled out as $^4[\text{AlVO}_4]^{+\bullet}$ is “only” 130 kJ mol^{-1} higher in energy than ground-state $^2[\text{AlVO}_4]^{+\bullet}$.
- [12] For selected reviews on FEL-IRPD, see: a) K. R. Asmis, J. Sauer, *Mass Spectrom. Rev.* **2007**, *26*, 542–562; b) K. R. Asmis, *Phys. Chem. Chem. Phys.* **2012**, *14*, 9270–9281; c) L. Jašíková, J. Roithová, *Chem. Eur. J.* **2018**, *24*, 3374–3390.

- [13] For an excellent essay on this approach entitled “High-Level Spectroscopy, Quantum Chemistry, and Catalysis: Not just a Passing Fad”, see: F. Neese, *Angew. Chem. Int. Ed.* **2017**, *56*, 11003–11010; *Angew. Chem.* **2017**, *129*, 11147–11154.
- [14] G. von Helden, A. Kirilyuk, D. van Heijnsbergen, B. Sartakov, M. A. Duncan, G. Meijer, *Chem. Phys.* **2000**, *262*, 31–39.
- [15] K. R. Asmis, G. Meijer, M. Brümmer, C. Kaposta, G. Santambrogio, L. H. Wöste, J. Sauer, *J. Chem. Phys.* **2004**, *120*, 6461–6470.
- [16] L. Jiang, T. Wende, P. Claes, S. Bhattacharyya, M. Sierka, G. Meijer, P. Lievens, J. Sauer, K. R. Asmis, *J. Phys. Chem. A* **2011**, *115*, 11187–11192.
- [17] N. Dietl, T. Wende, K. Chen, L. Jiang, M. Schlangen, X. Zhang, K. R. Asmis, H. Schwarz, *J. Am. Chem. Soc.* **2013**, *135*, 3711–3721.
- [18] X. Song, M. R. Fagiani, S. Gewinner, W. Schöllkopf, K. R. Asmis, F. A. Bischoff, F. Berger, J. Sauer, *J. Chem. Phys.* **2016**, *144*, 244305.
- [19] X. Song, M. R. Fagiani, S. Debnath, M. Gao, S. Maeda, T. Taketsugu, S. Gewinner, W. Schöllkopf, K. R. Asmis, A. Lyalin, *Phys. Chem. Chem. Phys.* **2017**, *19*, 23154–23161.
- [20] Actually, structure **6**·(CO)₆ should be better viewed as a complex of [AlVO₂]⁺ tagged with five CO and one CO₂ ligands. Thus, if this species was generated at all in the redox reaction, one would expect loss of *n* CO and CO₂ molecules upon photon absorption. However, this is not the case.
- [21] a) G. E. Johnson, R. Mitrić, E. C. Tyo, V. Bonačić-Koutecký, A. W. Castleman, Jr., *J. Am. Chem. Soc.* **2008**, *130*, 13912–13920; b) G. E. Johnson, R. Mitrić, M. Nöbler, E. C. Tyo, V. Bonačić-Koutecký, A. W. Castleman, Jr., *J. Am. Chem. Soc.* **2009**, *131*, 5460–5470; c) J.-B. Ma, Z.-C. Wang, M. Schlangen, S.-G. He, H. Schwarz, *Angew. Chem. Int. Ed.* **2013**, *52*, 1226–1230; *Angew. Chem.* **2013**, *125*, 1264–1268; d) J.-B. Ma, B. Xu, J.-H. Meng, X.-N. Wu, X.-L. Ding, X.-N. Li, S.-G. He, *J. Am. Chem. Soc.* **2013**, *135*, 2991–2998; e) X. Sun, S. Zhou, L. Yue, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2017**, *56*, 9990–9993; *Angew. Chem.* **2017**, *129*, 10122–10126.
- [22] For reviews, see: a) X.-L. Ding, X.-N. Wu, Y.-X. Zhao, S.-G. He, *Acc. Chem. Res.* **2012**, *45*, 382–390; b) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5544–5555; *Angew. Chem.* **2012**, *124*, 5638–5650; c) W. Lai, C. Li, H. Chen, S. Shaik, *Angew. Chem. Int. Ed.* **2012**, *51*, 5556–5578; *Angew. Chem.* **2012**, *124*, 5652–5676; d) H. Schwarz, *Isr. J. Chem.* **2014**, *54*, 1413–1431; e) H. Schwarz, S. Shaik, J. Li, *J. Am. Chem. Soc.* **2017**, *139*, 17201–17212.
- [23] Note added in proof (16 May 2018): Dr. A. Viggiano has informed us (15 May 2018) about his experimental/computational studies on the role of non-reactive binding sites in the [AlVO_x]⁺/CO/N₂O (*x* = 3, 4) redox systems. In line with our findings, the Al–O_i site constitutes the active center, and (unproductive) complexation of the vanadium site by N₂O is the root cause for the reduced efficiency of the redox process.
- [24] For many references, see: J. Li, P. González-Navarrete, M. Schlangen, H. Schwarz, *Chem. Eur. J.* **2015**, *21*, 7780–7789.