Freie Universität Berlin

Spectroscopy of Metal Oxide Ions: A Progress Report …

on deciphering a reaction mechanism.

Torsten Siebert

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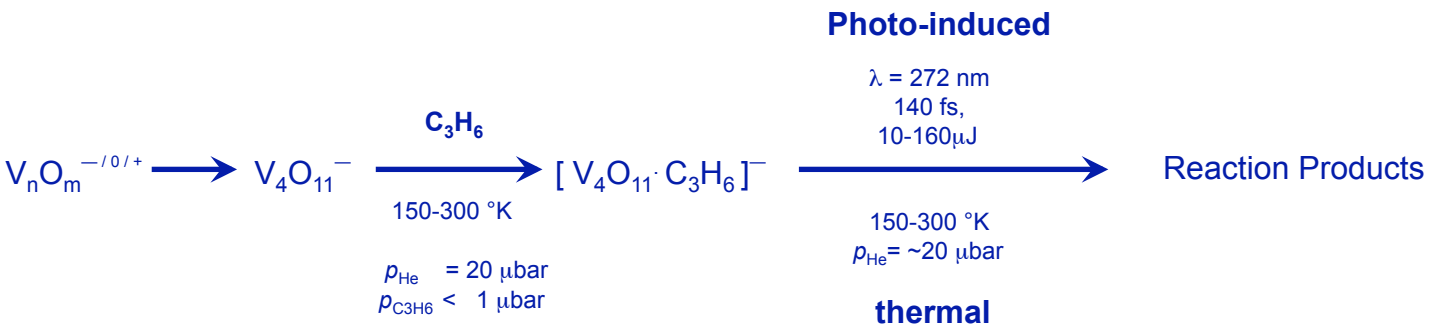
Photo-induced
λ = 272 nm
140 fs,
10-160μJ
$V_nO_m^{-/0/+}$
$V_4O_{11}^-$
C_3H_6
150-300 °K
$[V_4O_{11}\cdot C_3H_6]^-$
150-300 °K
p_{He} = 20 μbar
p_{C3H6} < 1 μbar
p_{He}= ~20 μbar
thermal
Reaction Products

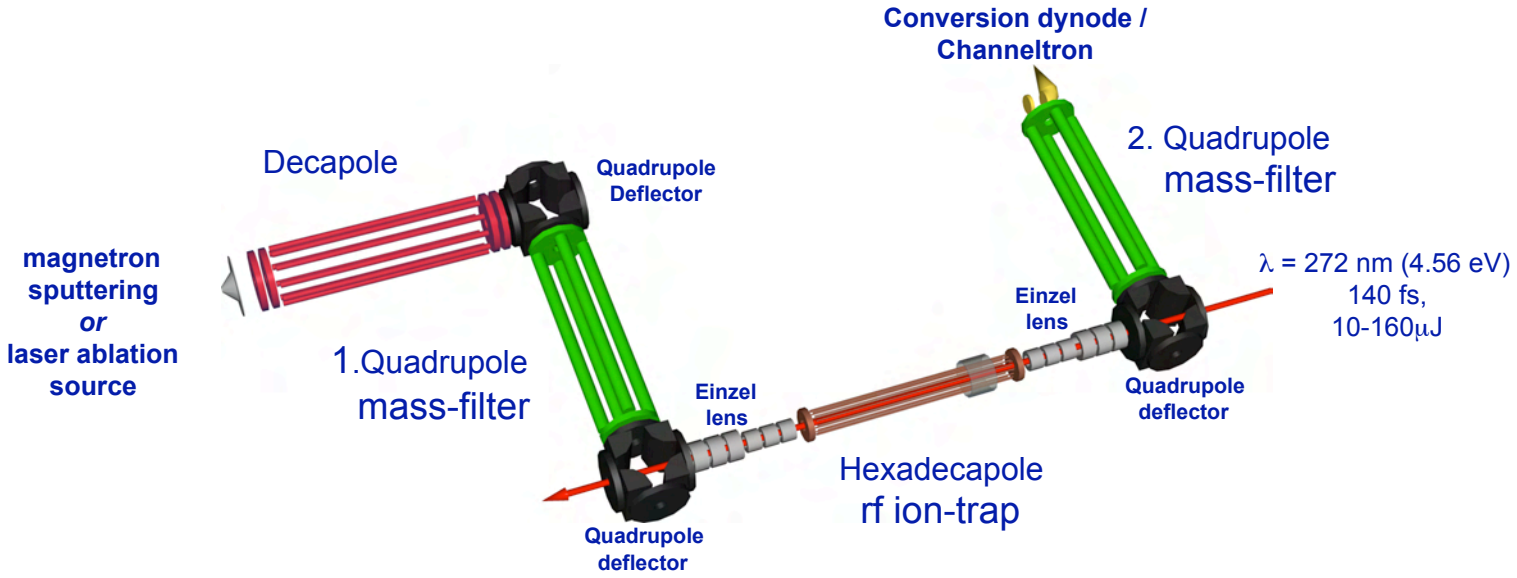
Conversion dynode /
Channeltron
2. Quadrupole
mass-filter
Decapole
Quadrupole
Deflector
magnetron
sputtering
or
laser ablation
source
λ = 272 nm (4.56 eV)
140 fs,
10-160μJ
Einzel
lens
1.Quadrupole
mass-filter
Einzel
lens
Quadrupole
deflector
Hexadecapole
rf ion-trap
Quadrupole
deflector

Photo-induced

$V_nO_m^{-/0/+}$ → $V_4O_{11}^-$ —(C_3H_6, 150-300 °K; p_{He} = 20 μbar, p_{C3H6} < 1 μbar)→ $[V_4O_{11}\cdot C_3H_6]^-$ —(λ = 272 nm, 140 fs, 10-160μJ; 150-300 °K, p_{He} = ~20 μbar; **thermal**)→ Reaction Products

PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

Gas phase vibrational spectroscopy of mass-selected vanadium oxide anions†

Gabriele Santambrogio,[a] Mathias Brümmer,[a] Ludger Wöste,[a] Jens Döbler,[b] Marek Sierka,[b] Joachim Sauer,*[b] Gerard Meijer[c] and Knut R. Asmis*[c]

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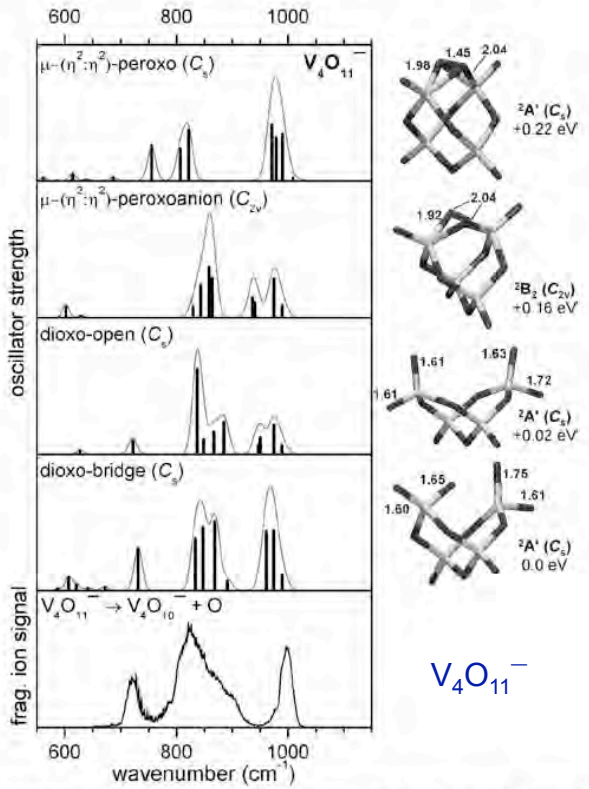
DOI: 10.1039/b803492c

$V_4O_{10}^-$

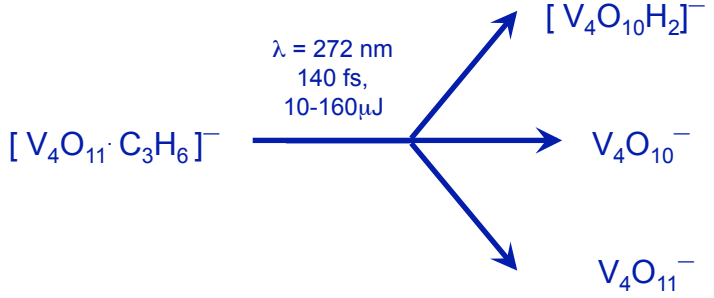
oxygen atom insertion →



$V_4O_{11}^-$

Fig. 6 Experimental IRMPD spectrum (bottom) of $V_4O_{11}^-$ and simulated linear IR absorption spectra, based on scaled B3LYP/TZVP frequencies and oscillator strengths of four low energy isomers for $V_4O_{11}^-$. Optimized structures, including characteristic bonds lengths (in Å) and relative energies with respect to the ground state, are shown to the right of the spectra. Data in part shown previously in ref. 22.

Photo-induced reaction



oxygen transfer + dehydrogenation

oxygen transfer

dissociation

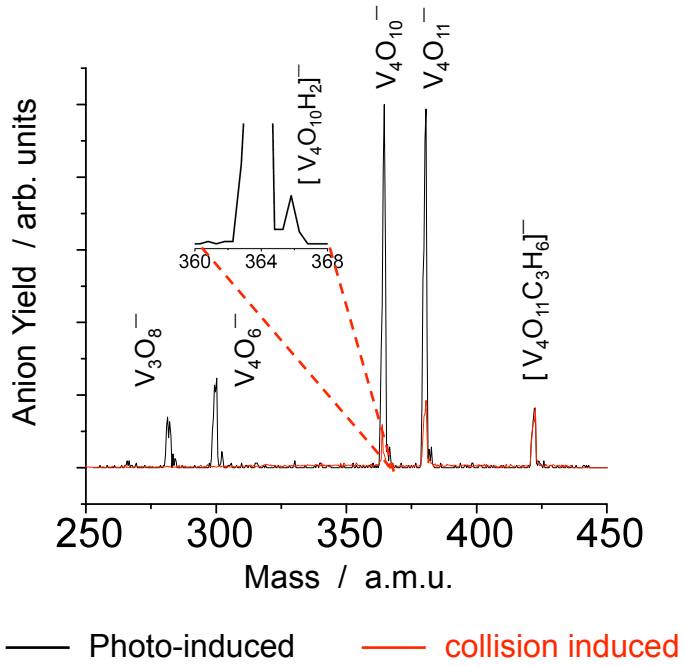
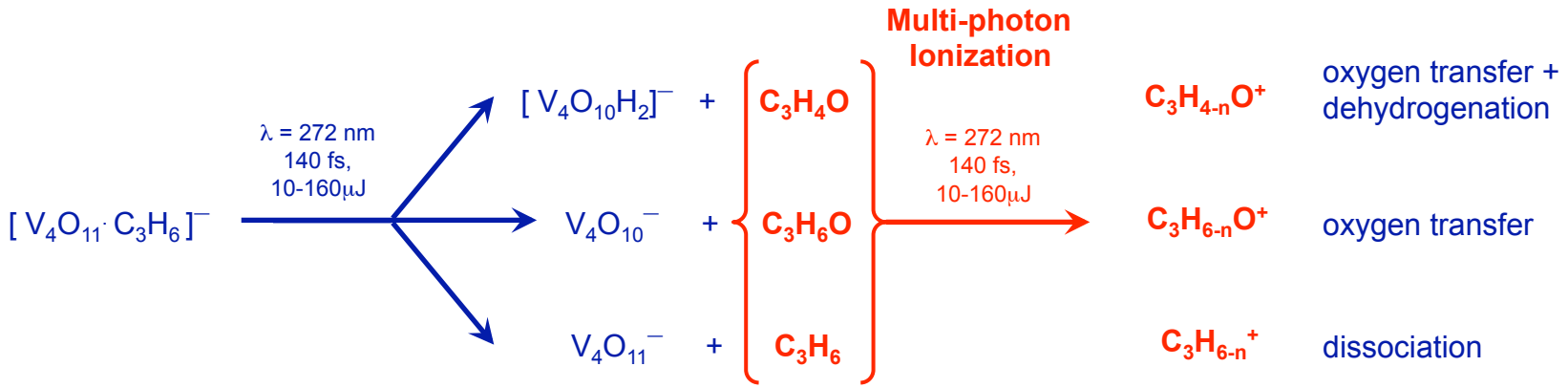
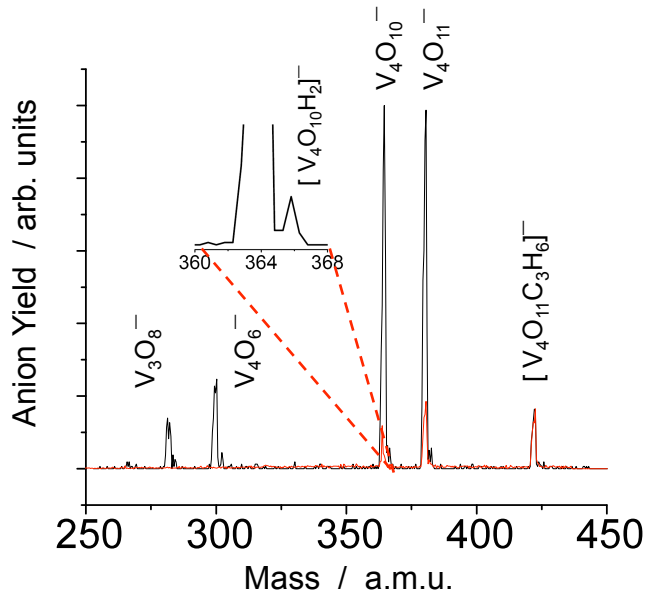


Photo-induced reaction





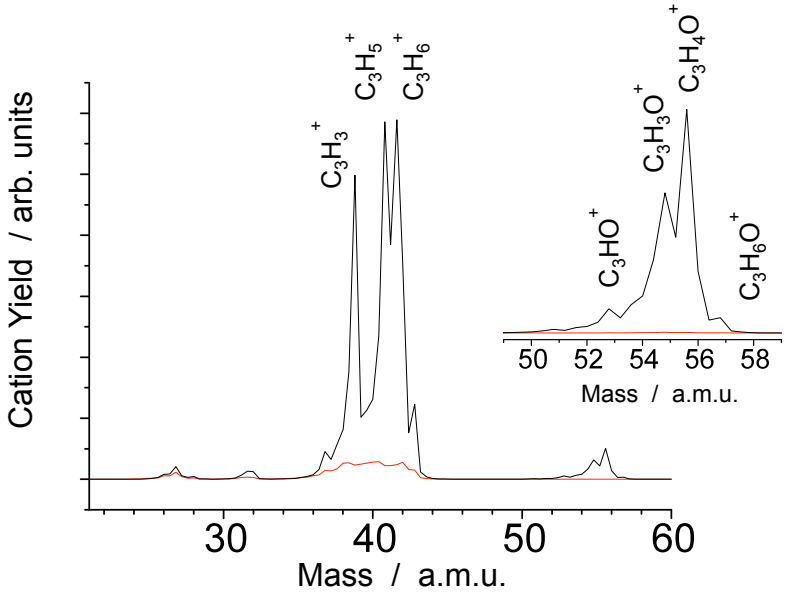
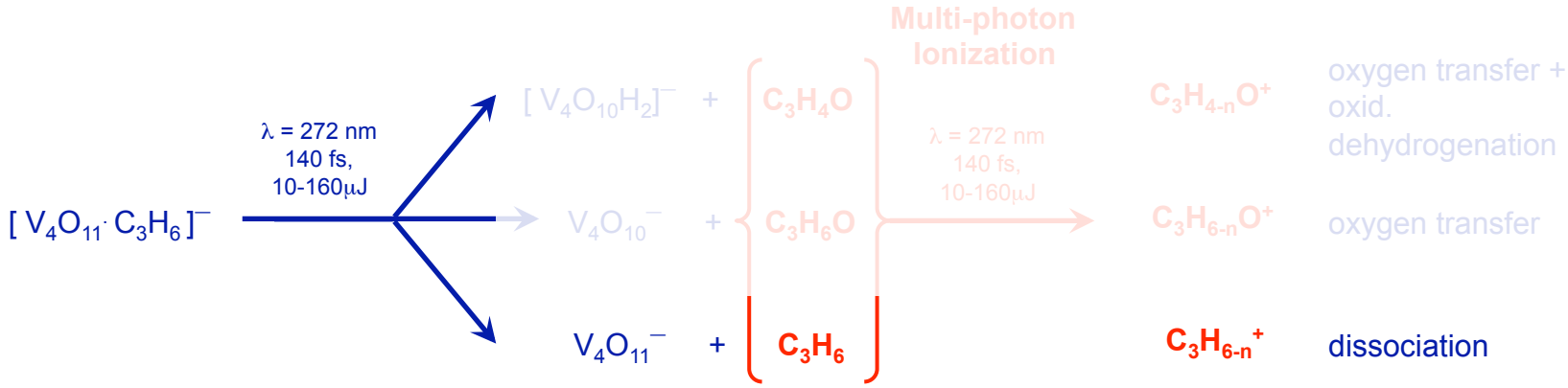
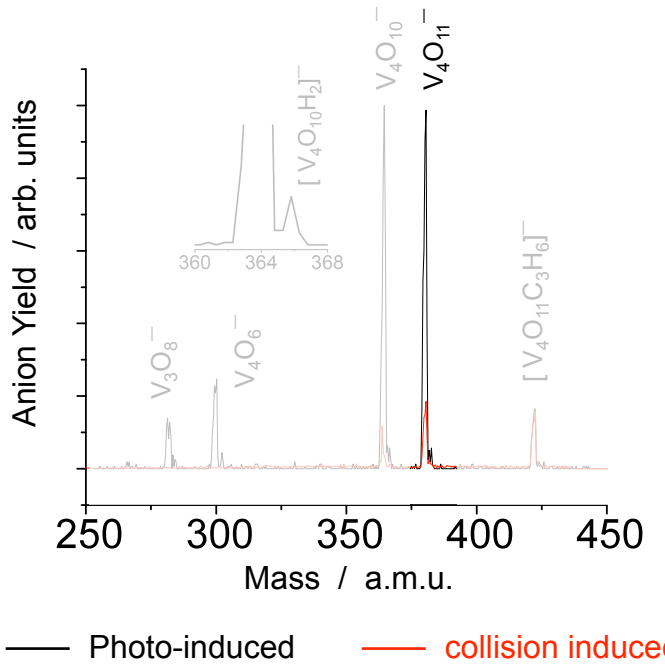


Photo-induced — collision induced

with $V_4O_{11}^-$ — without $V_4O_{11}^-$

Photo-induced reaction





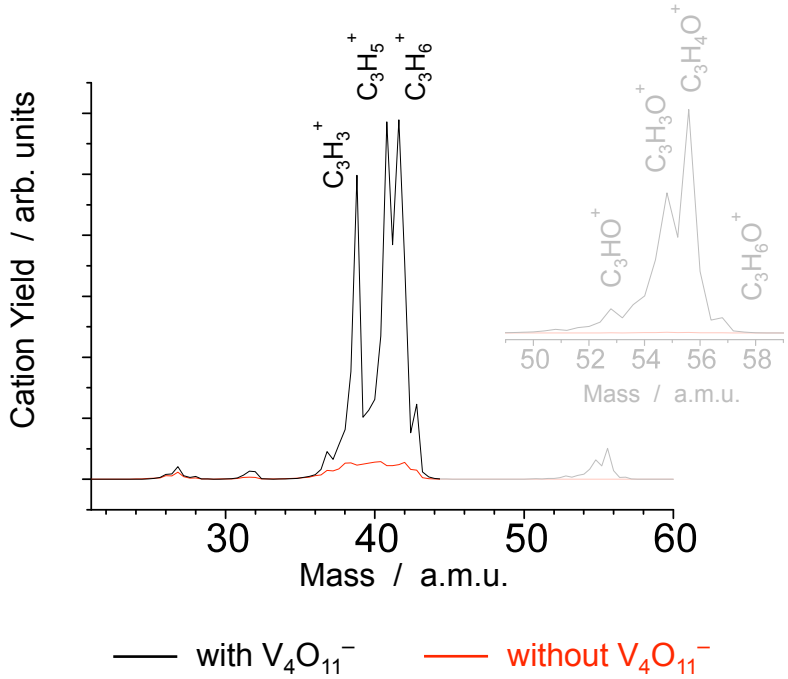
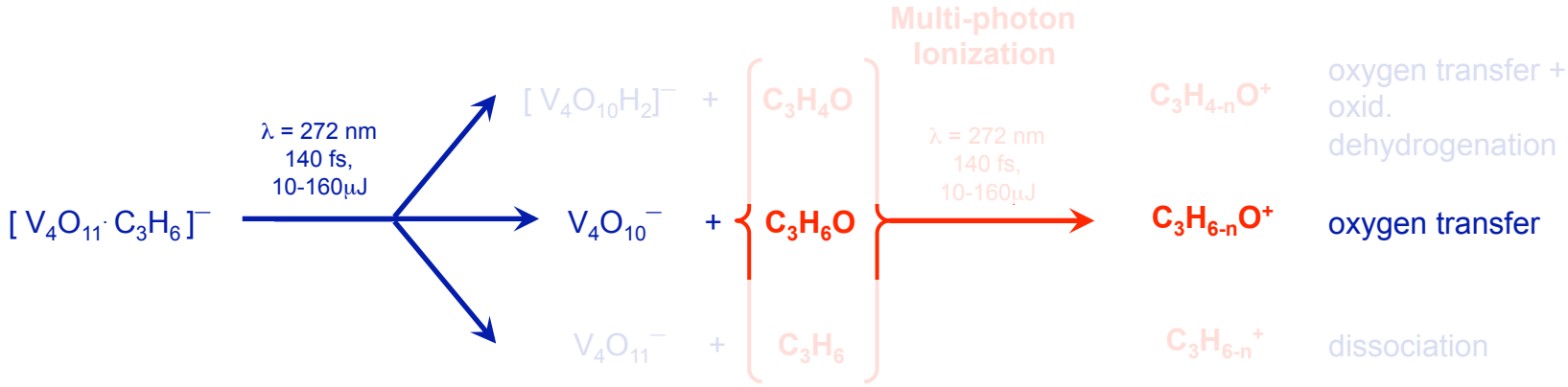
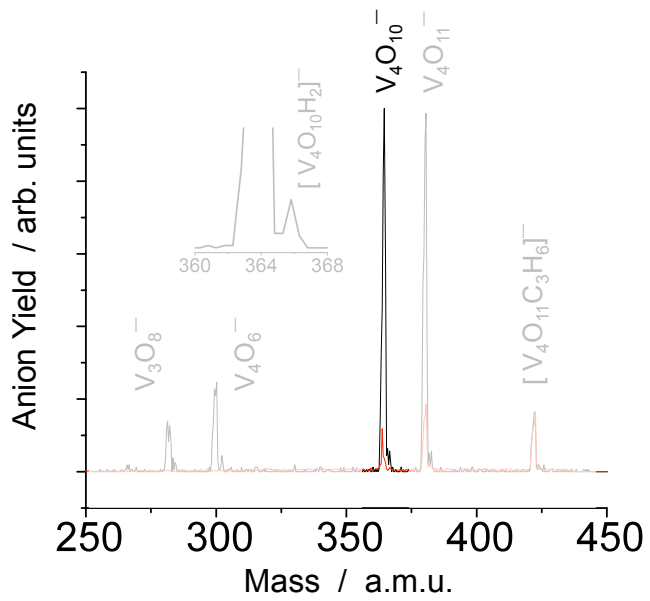


Photo-induced reaction





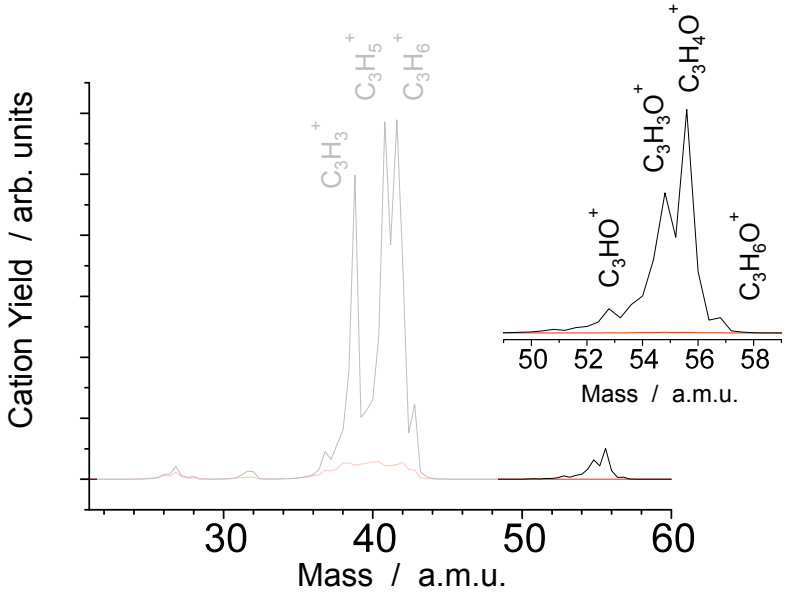
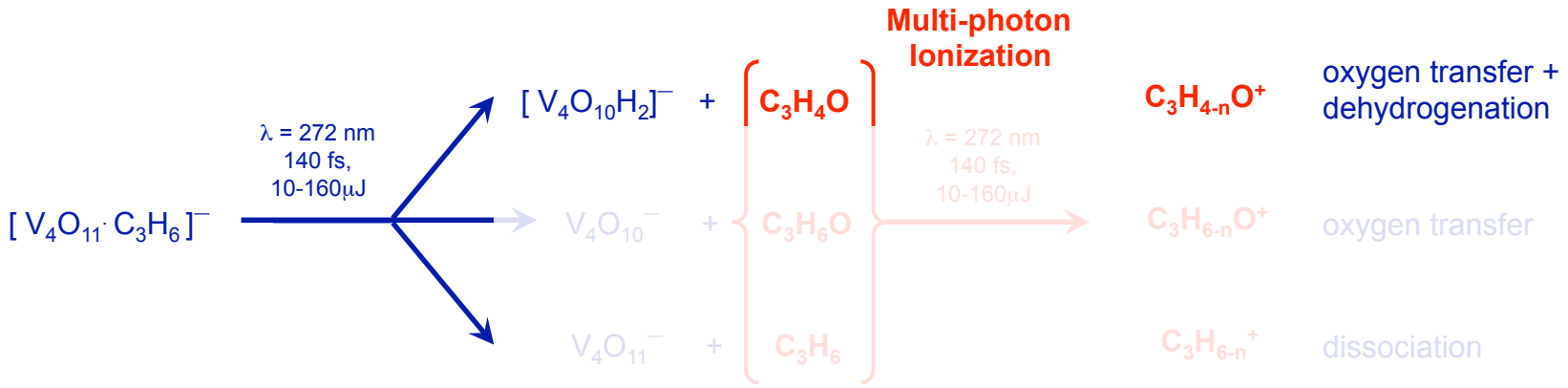
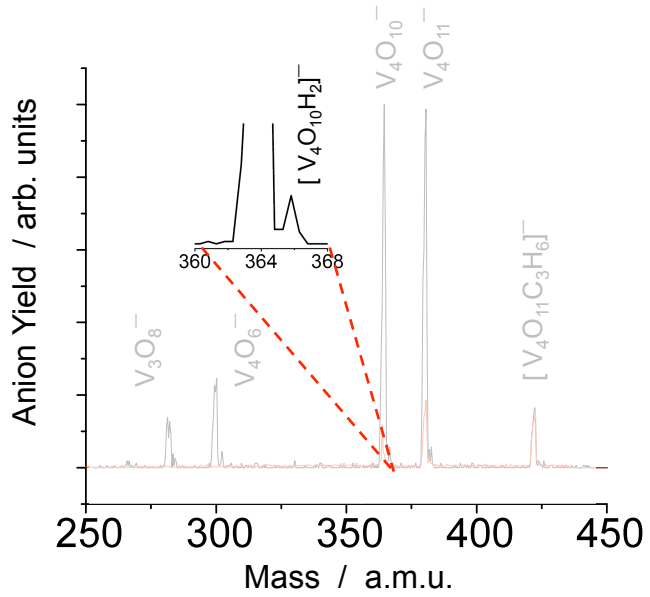


Photo-induced — collision induced

with $V_4O_{11}^-$ — without $V_4O_{11}^-$

Photo-induced reaction





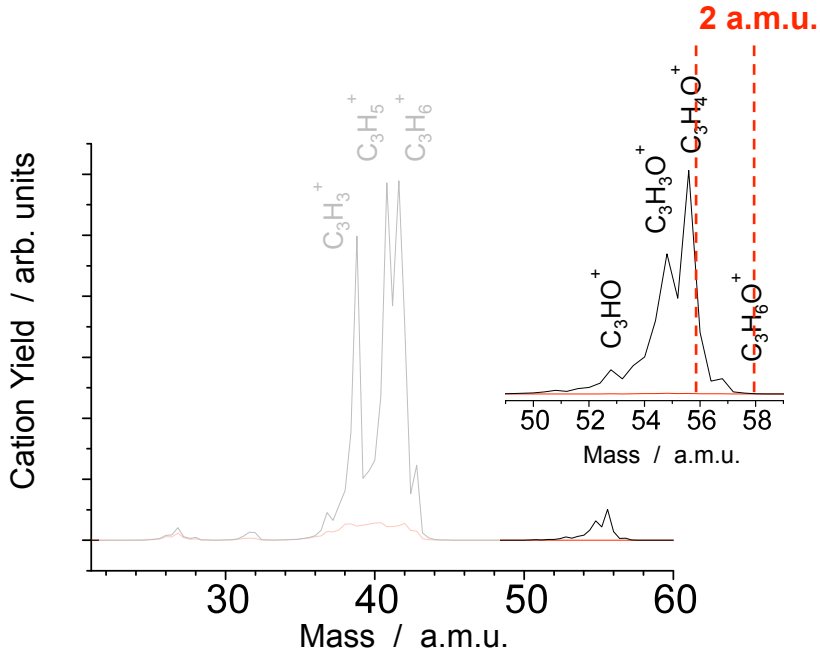
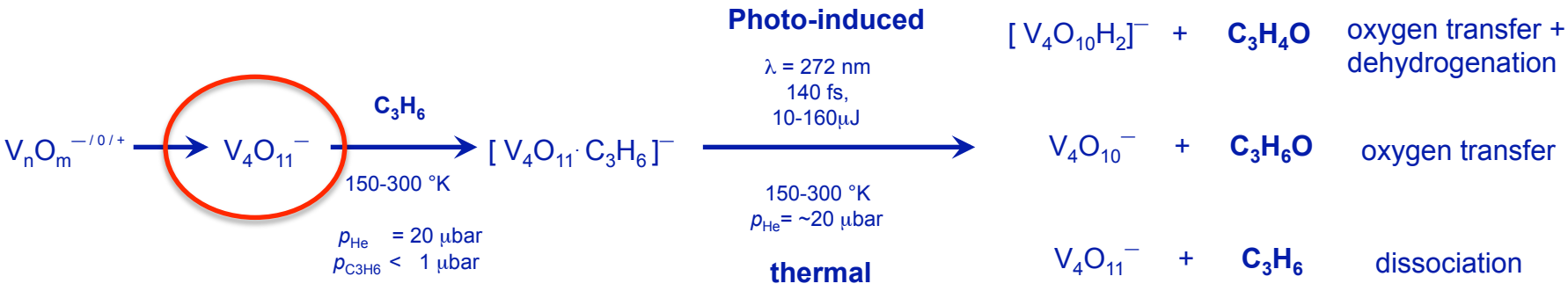
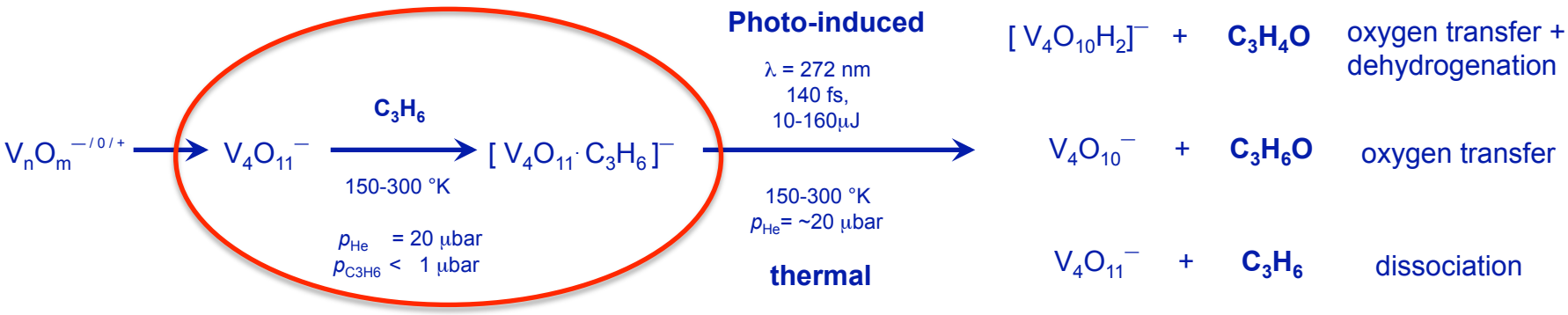


Photo-induced — collision induced

with $V_4O_{11}^-$ — without $V_4O_{11}^-$

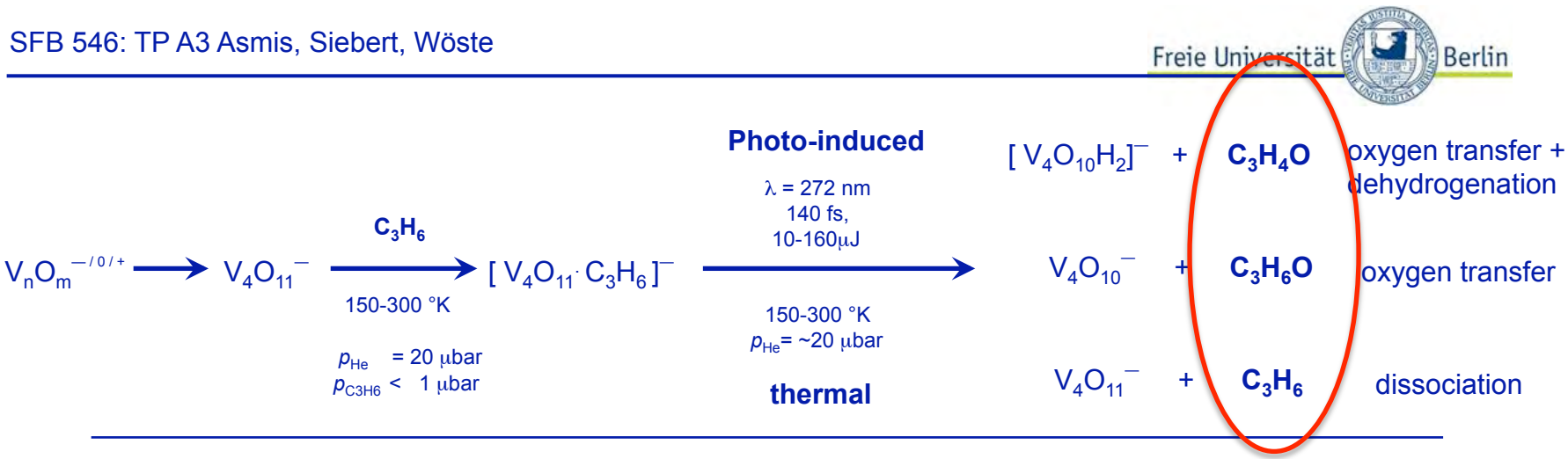


1. Photo-active structural unit ?

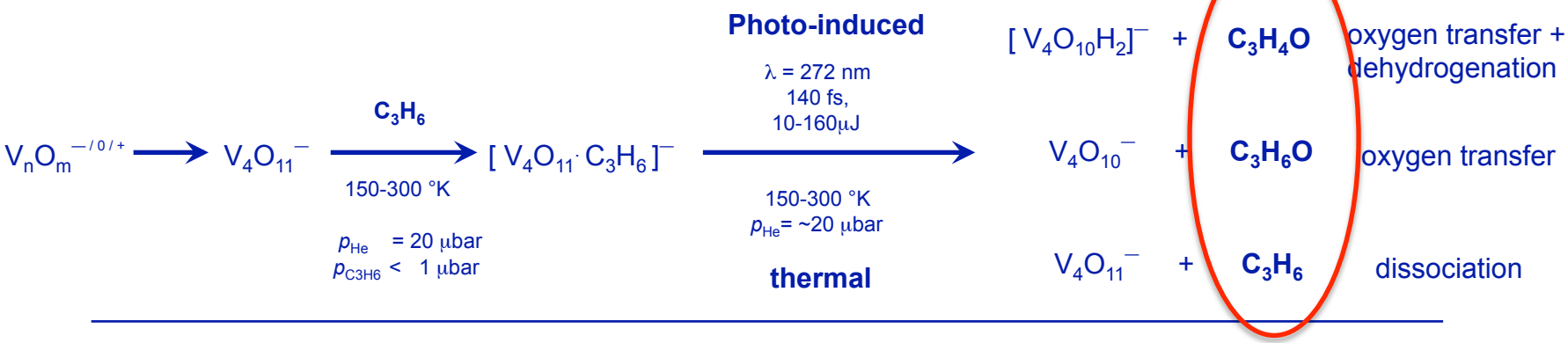


1. **Photo-active structural unit ?**

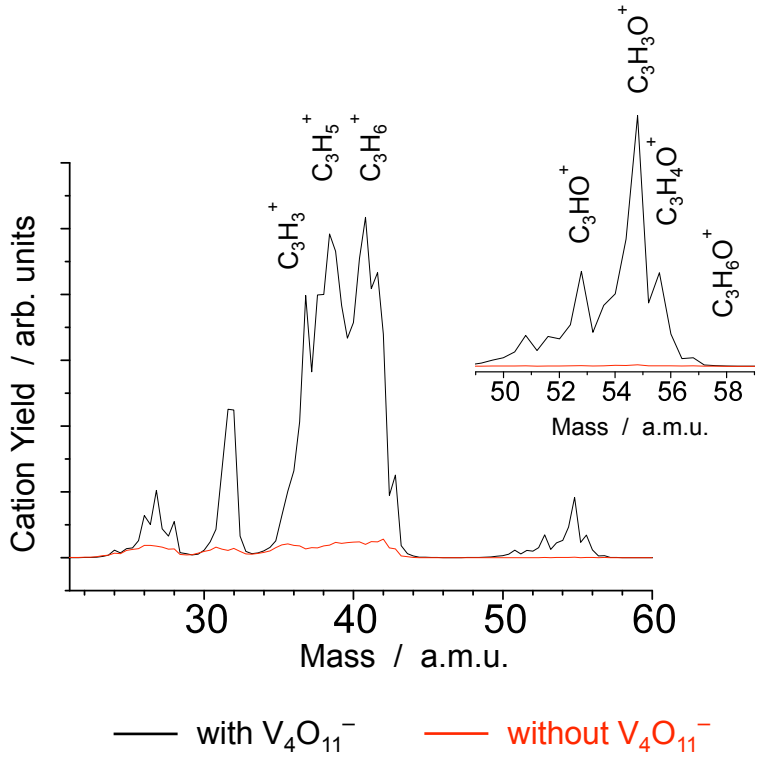
2. **Reaction complex: nature and mechanism of formation ?**



1. **Photo-active structural unit ?**
2. **Reaction complex: nature and mechanism of formation ?**
3. **Nature of the reaction product(s) ?**



3. Nature of the reaction product(s) ?



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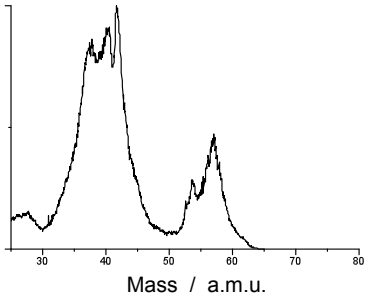
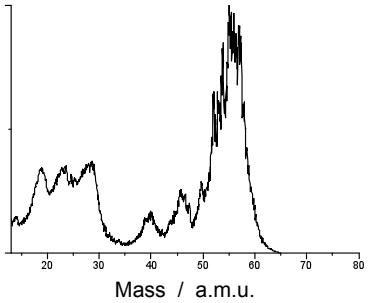
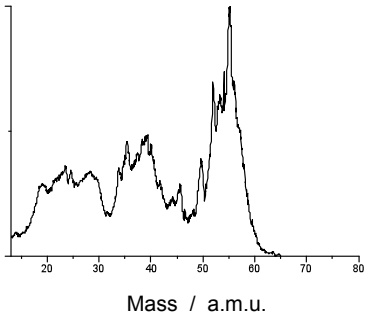
Aceton



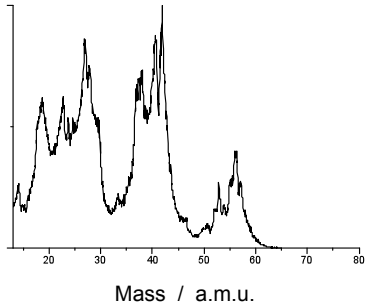
Propionaldehyd



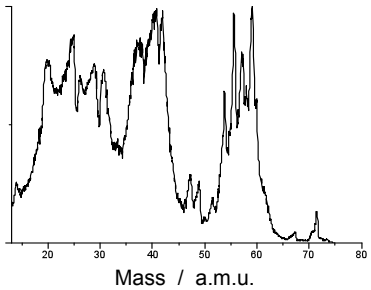
Allylalkohol



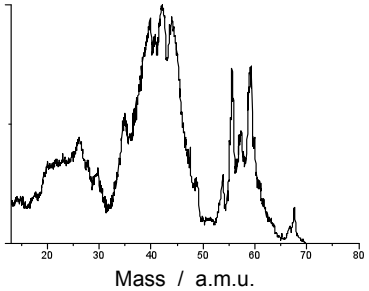
Propylenoxid



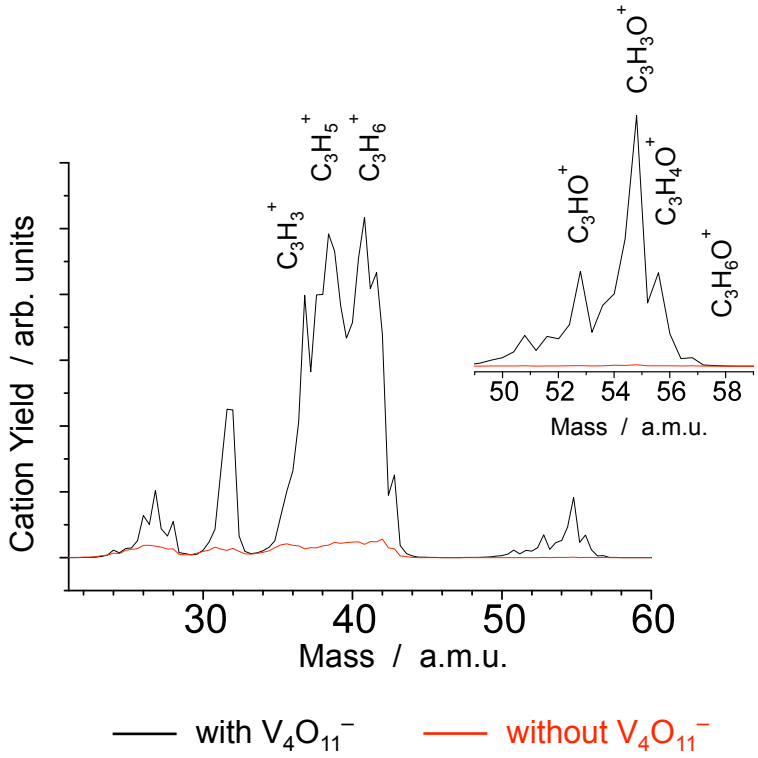
1-Propanol



2-Propanol

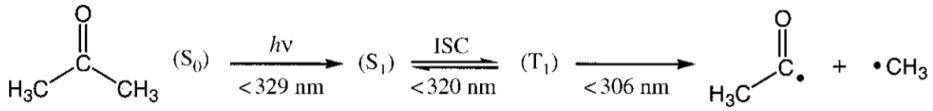


Reaction Product



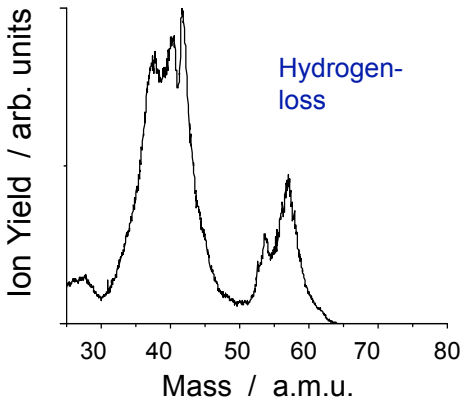
Femtochemistry of Norrish Type-I Reactions: I. Experimental and Theoretical Studies of Acetone and Related Ketones on the S_1 Surface

Eric W.-G. Diau, Carsten Kötting, and Ahmed H. Zewail*[a]



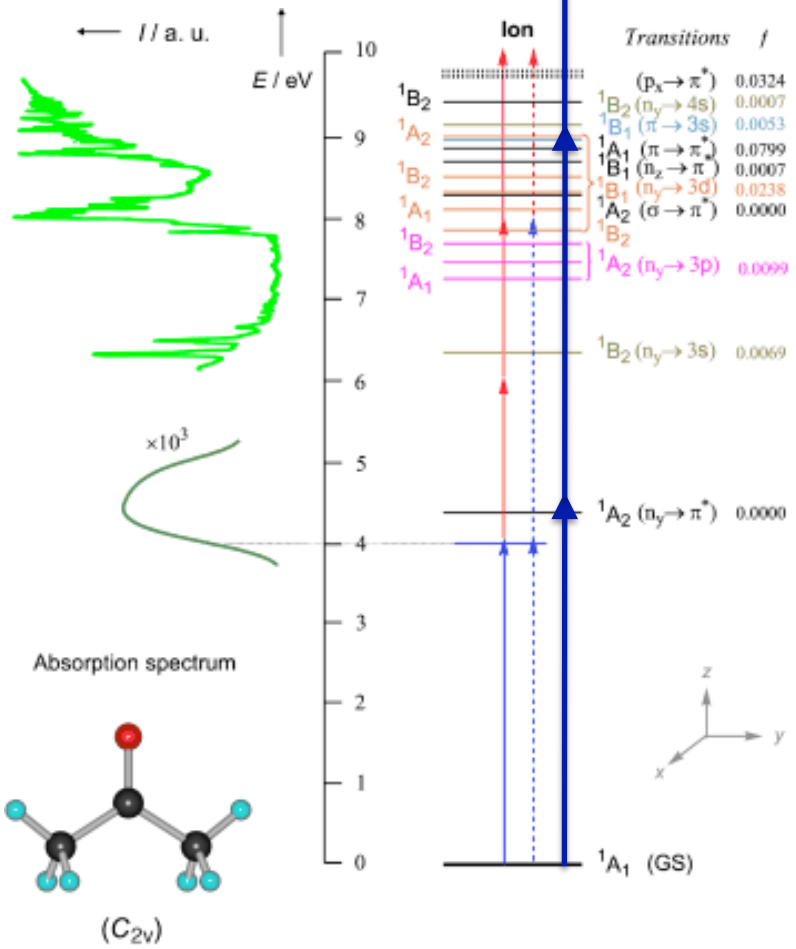
Methyl-loss

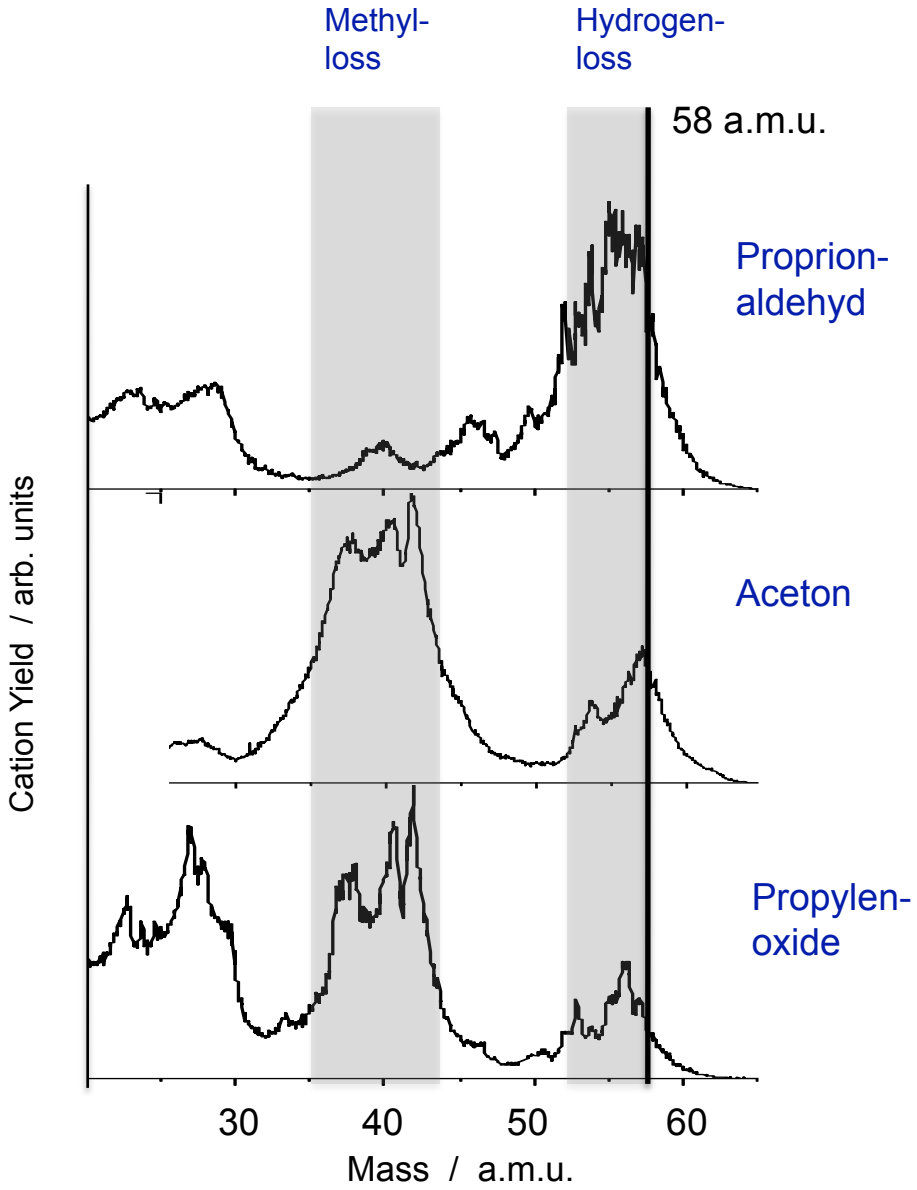
Aceton

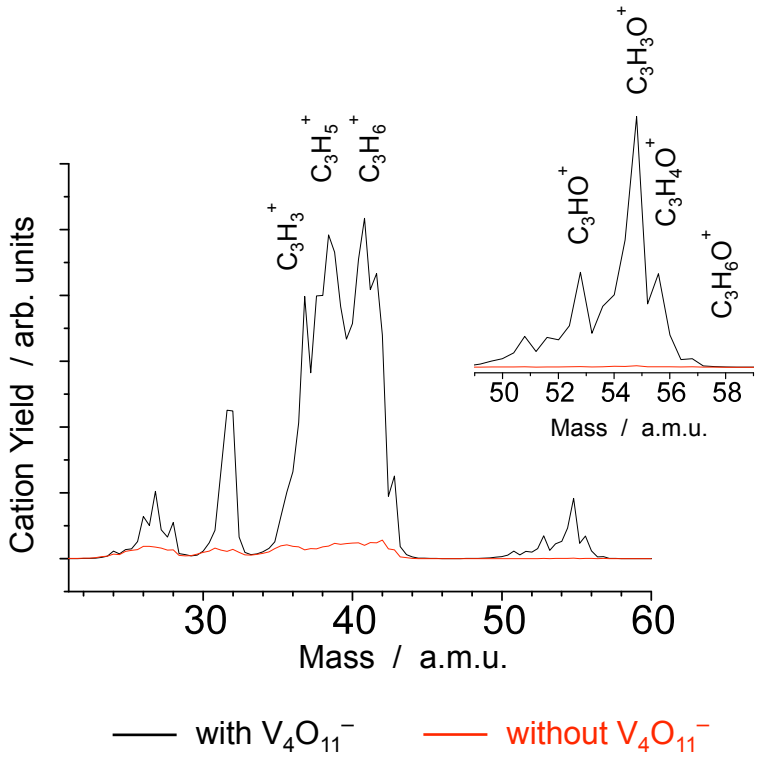


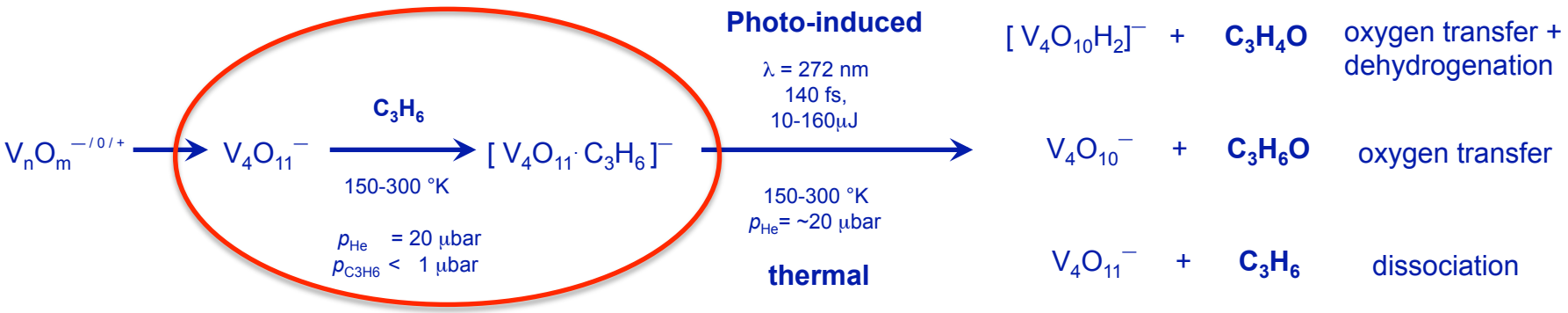
3 x 272 nm
(3 x 4.55 eV)

Above Threshold Ionization

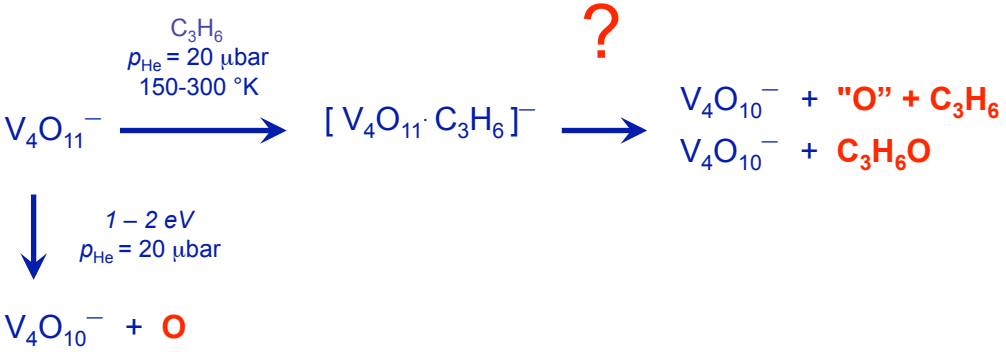


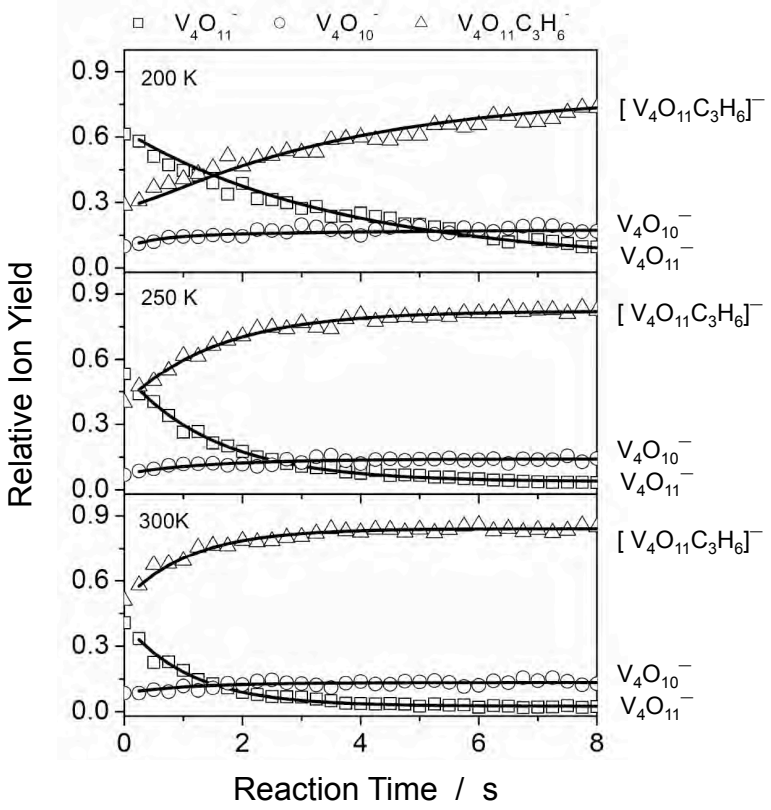

Methyl-
loss
Hydrogen-
loss
58 a.m.u.
Proprion-
aldehyd
Aceton
Propylen-
oxide
Cation Yield / arb. units
30
40
50
60
Mass / a.m.u.

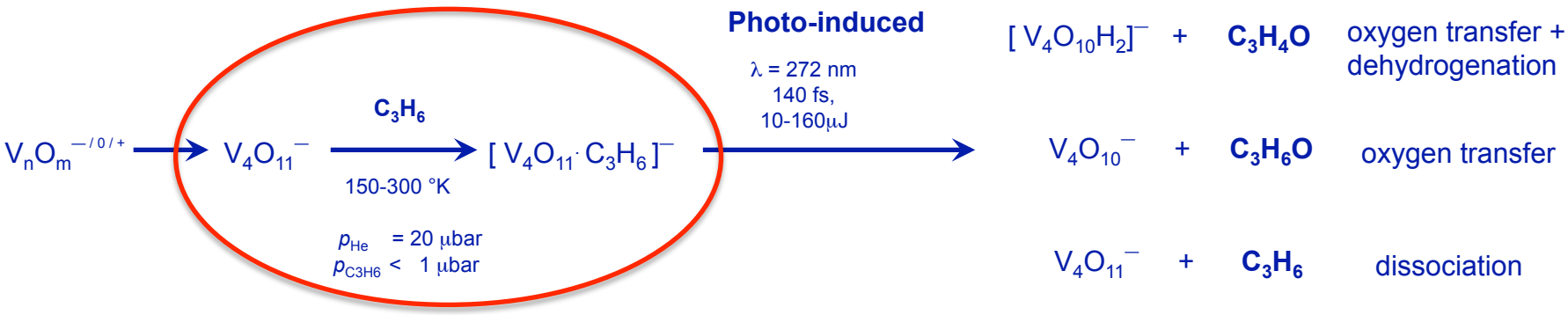

$C_3H_3^+$
$C_3H_5^+$
$C_3H_6^+$
C_3HO^+
$C_3H_4O^+$
$C_3H_3O^+$
$C_3H_6O^+$
Cation Yield / arb. units
30
40
50
60
Mass / a.m.u.
50
52
54
56
58
Mass / a.m.u.
with $V_4O_{11}^-$
without $V_4O_{11}^-$



2. Reaction complex: nature and mechanism of formation ?







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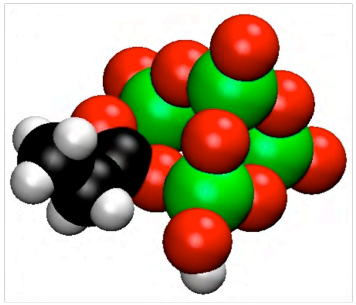
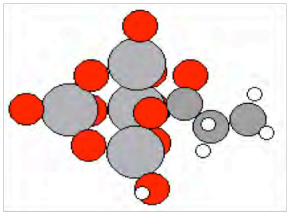


Structure I

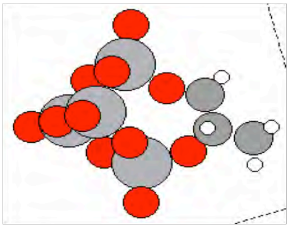
?

Structure I



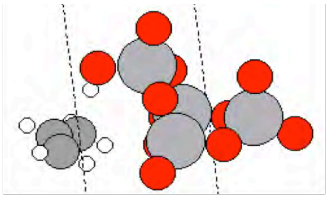
BE PBE (3.17 eV)
BE TPSS (2.97 eV)
BE M06-L (4.03 eV)

Structure II

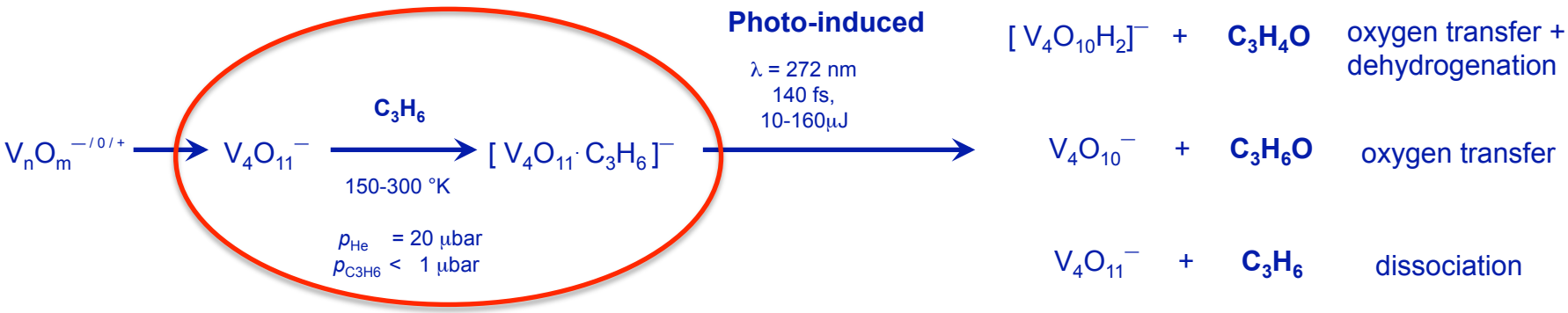


BE PBE (3.64 eV)

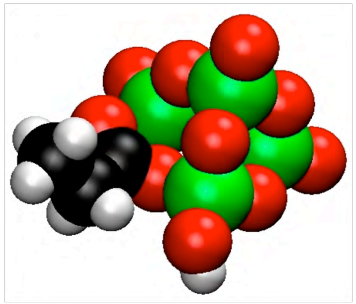
Structure III



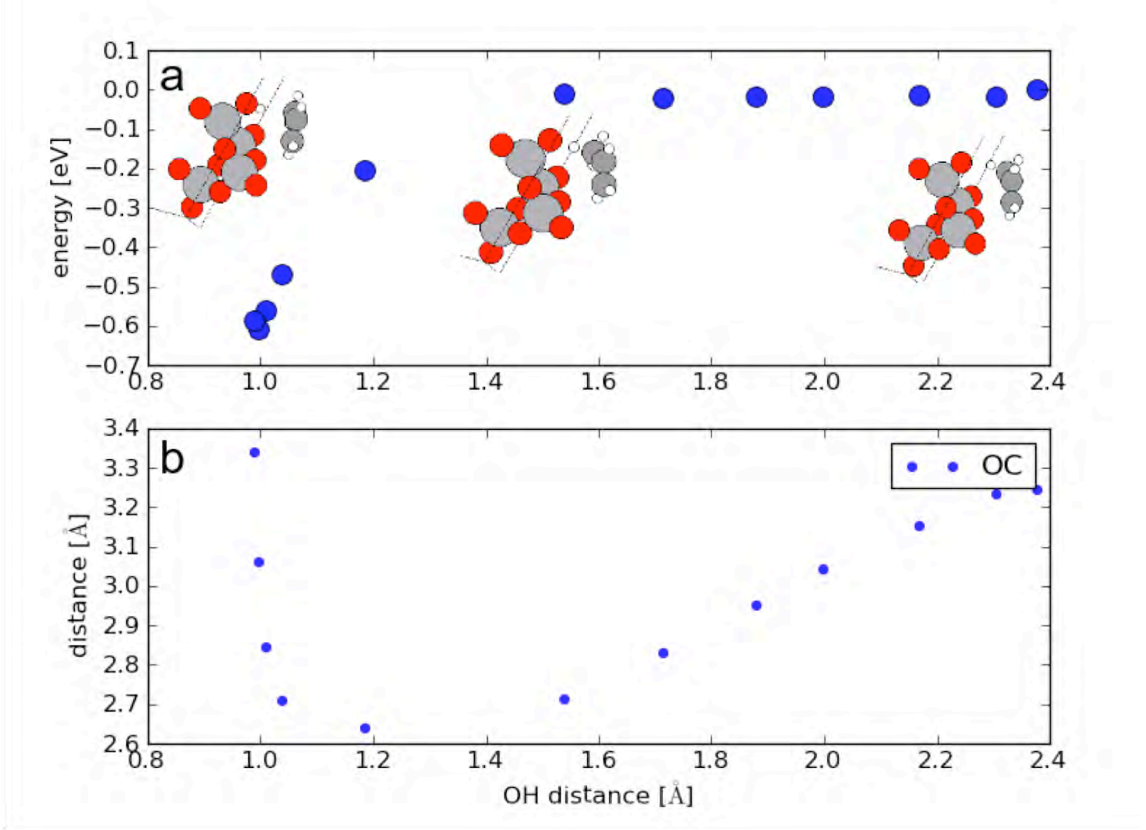
BE PBE (1.67 eV)

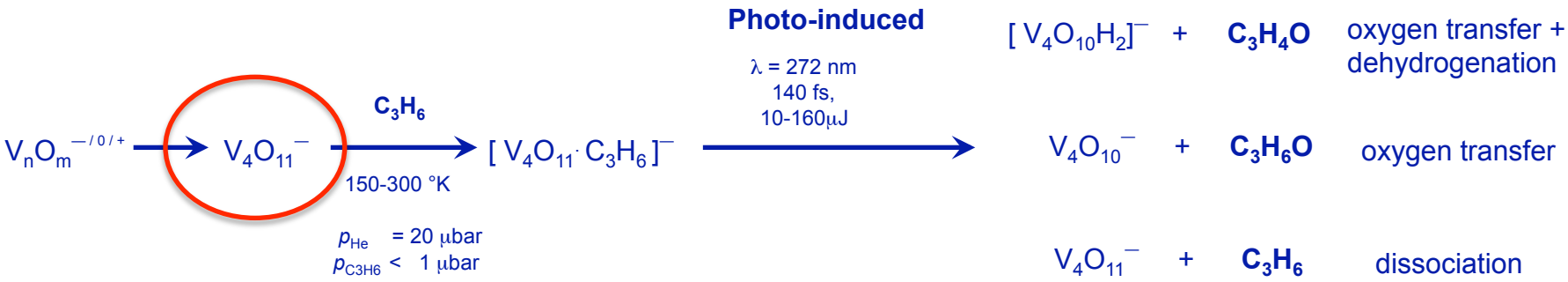


2. Reaction complex: nature and mechanism of formation ?



Structure
I





1. Photo-active structural unit ?

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Gas phase vibrational spectroscopy of mass-selected vanadium oxide anions†

Gabriele Santambrogio,[a] Mathias Brümmer,[a] Ludger Wöste,[a] Jens Döbler,[b] Marek Sierka,[b] Joachim Sauer,*[b] Gerard Meijer[c] and Knut R. Asmis*[c]

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DOI: 10.1039/b803492c

vanadyl- ***versus*** peroxo- or dioxo-

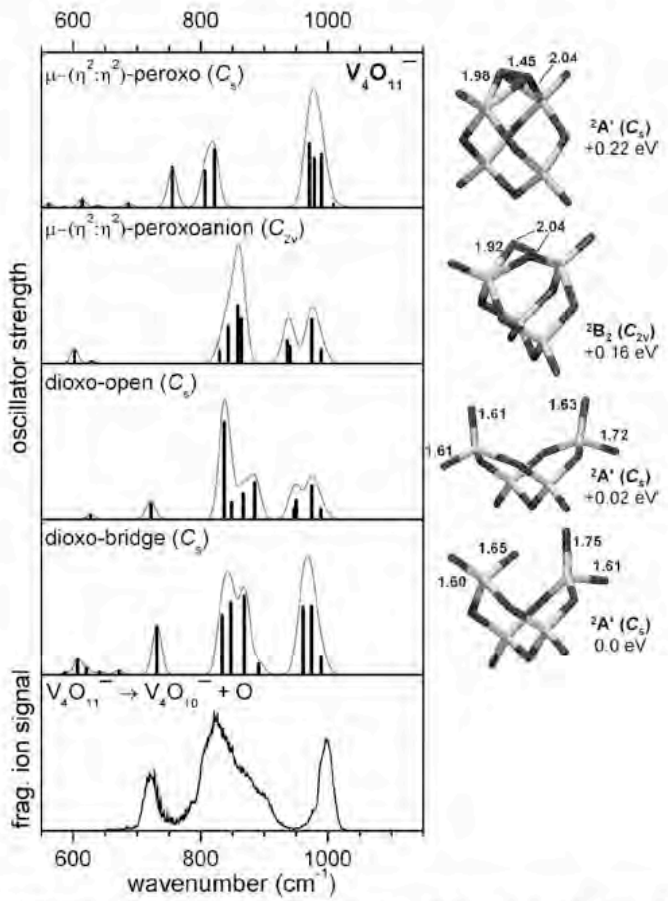
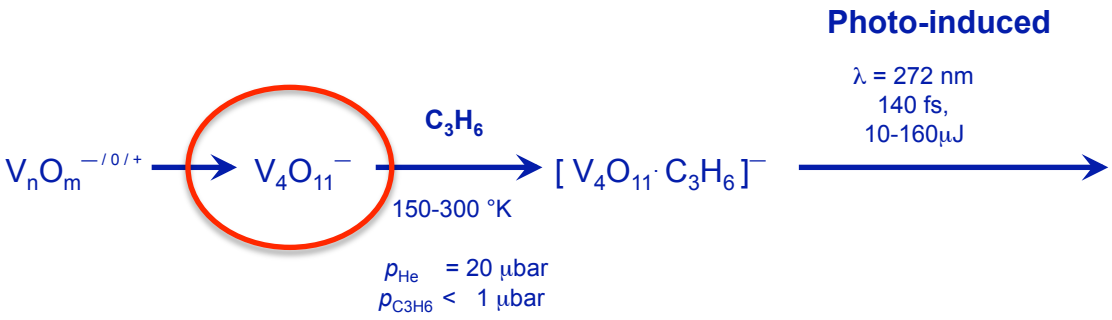
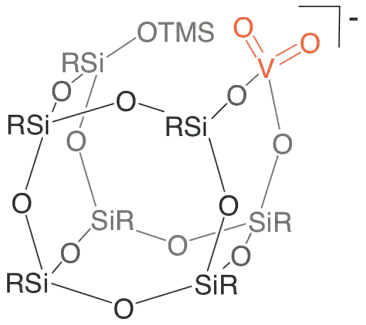


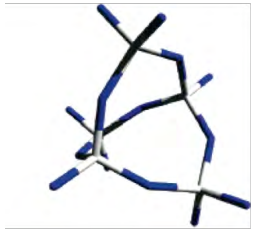
Fig. 6 Experimental IRMPD spectrum (bottom) of $V_4O_{11}^-$ and simulated linear IR absorption spectra, based on scaled B3LYP/TZVP frequencies and oscillator strengths of four low energy isomers for $V_4O_{11}^-$. Optimized structures, including characteristic bonds lengths (in Å) and relative energies with respect to the ground state, are shown to the right of the spectra. Data in part shown previously in ref. 22.



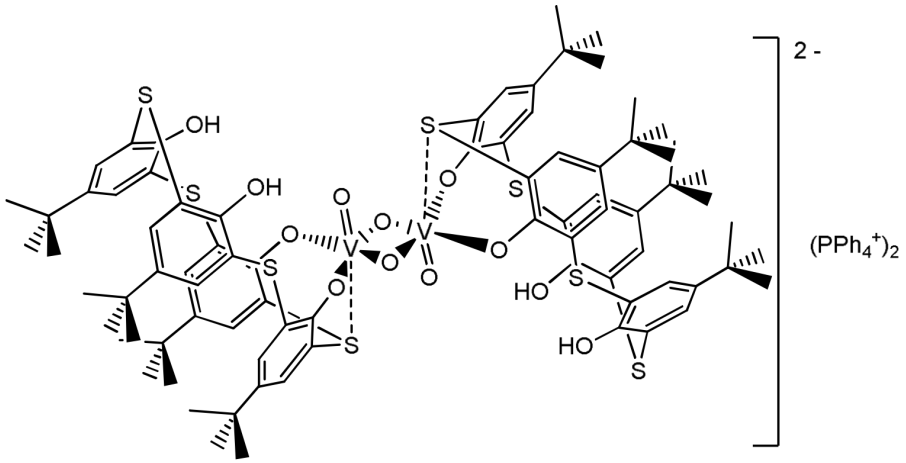
1. Photo-active structural unit ?

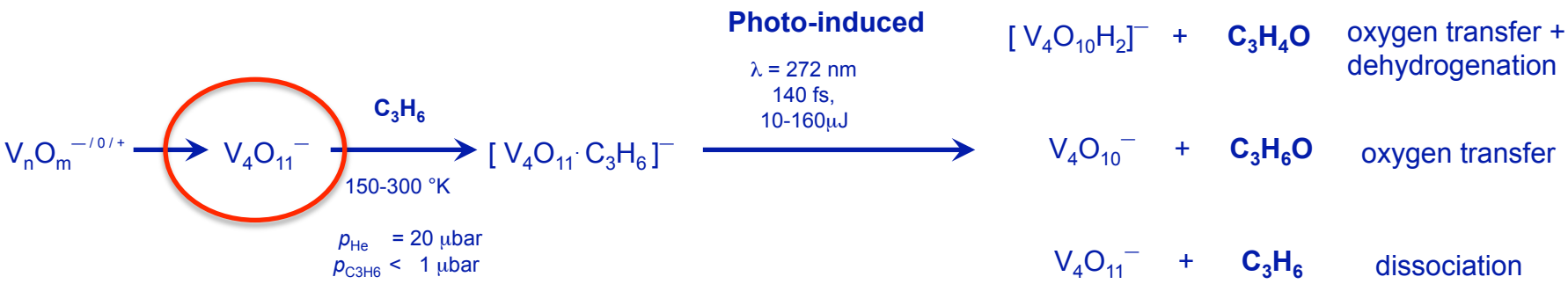


Silsesquioxanes
(R = isobutyl)

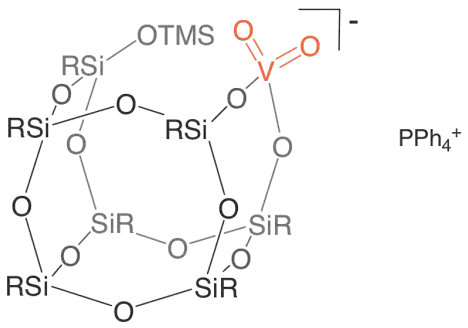


$(NH_4)_3[V_5O_{14}]$

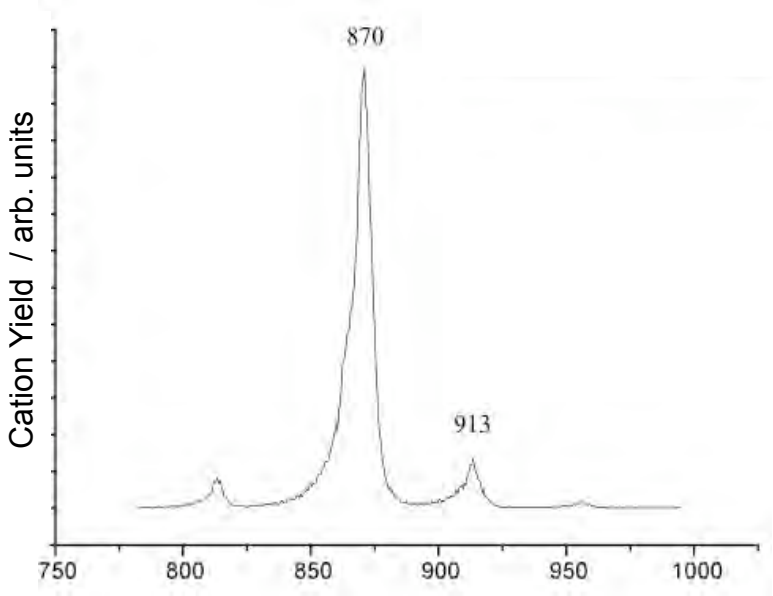




1. Photo-active structural unit ?



Silsesquioxanes
(R = isobutyl)



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