

Manuscript: jp-2012-046142

Submitted to the *J. Phys. Chem. A* Peter B. Armentrout Festschrift.

REVISED Version: 11 July 2012

Guest Editors: Profs. Mary T. Rodgers and Kent Ervin.

Handling Editor: Prof. Michael A. Duncan.

Supplementary Materials

Gas-Phase Reactions of $[\text{VO}_2(\text{OH})_2]^-$ and $[\text{V}_2\text{O}_5(\text{OH})]^-$ with Methanol: Experiment and Theory[‡]

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[‡] Dedicated to our friend and colleague Peter B. Armentrout on the occasion of his 60th birthday, and in recognition of his outstanding work in metal mediated chemistry, which has been an ongoing source of inspiration.

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Full citation details for reference #24:

Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.

Table S1: Calculated reaction rates for the reaction of $[V_2O_5(OH)]^-$ with MeOH

Run number	Calculated Rate ($\text{Cm}^3/\text{molecules.s}$)	ADO rate
1	7.355*E-11	1.4519*E-9
2	2.517*E-10	
1	3.510*E-10	
2	1.654*E-10	
1	1.672*E-10	
2	1.400*E-10	
3	0.991*E-10	
4	1.128*E-10	
5	2.417*E-10	
6	3.332*E-10	
Average Rate	1.935*E-10	
Standard Deviation	0.967 *E-10	
Reaction Efficiency	13.30% $\pm$ 6.6	

^a Units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Reaction efficiency (φ) = $k/k_{\text{ADO}} \times 100$.

The ADO collision rate was calculated using the theory of Chesnavich et al [1]. The calculation was performed using the program COLRATE [2].

[1] Chesnavich, W.J.; Su, T.; Bowers, M.T., *J. Chem. Phys.*, **1980**, 72, 2641.

[2] Lim, K.F. Quantum Chemistry Program Exchange, **1994**, 14, 3.

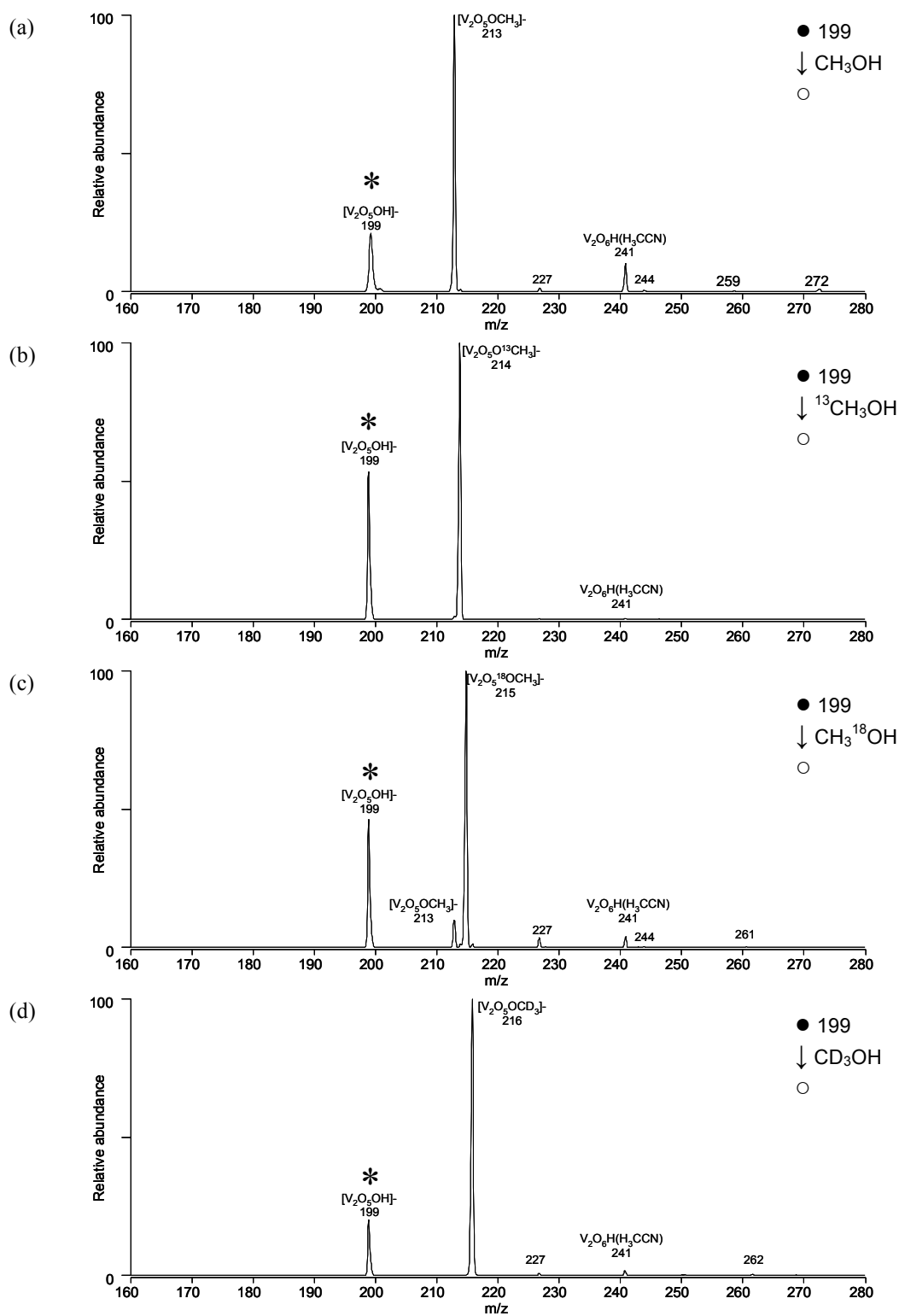


Fig. S1: Ion-molecule reaction (MS^2) of $[V_2O_5(OH)]^-$ (**2**) with labelled methanol: (a) CH₃OH, (b) ¹³CH₃OH, (c) CH₃¹⁸OH and (d) CD₃OH. Mass selected precursor indicated by *.

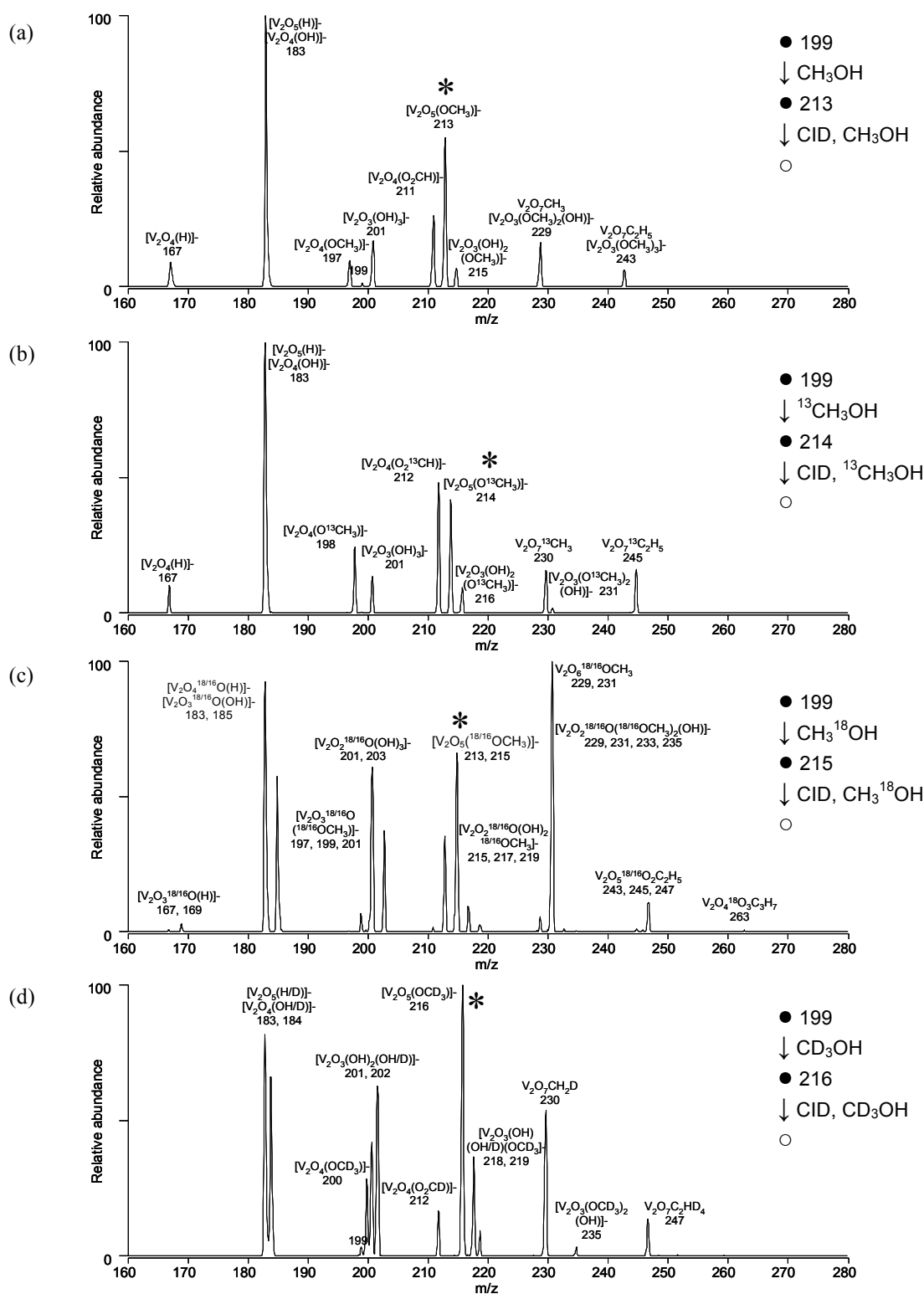


Fig. S2: Collision induced dissociation (MS^3) of labelled $[V_2O_5(OCH_3)]^-$ (7) in the presence of labelled methanol: (a) $[V_2O_5(OCH_3)]^-$ + CH_3OH , (b) $[V_2O_5(O^{13}CH_3)]^-$ + $^{13}CH_3OH$, (c) $[V_2O_5(^{18}OCH_3)]^-$ + $CH_3^{18}OH$ and (d) $[V_2O_5(OCD_3)]^-$ + CD_3OH . Mass selected precursor indicated by *.

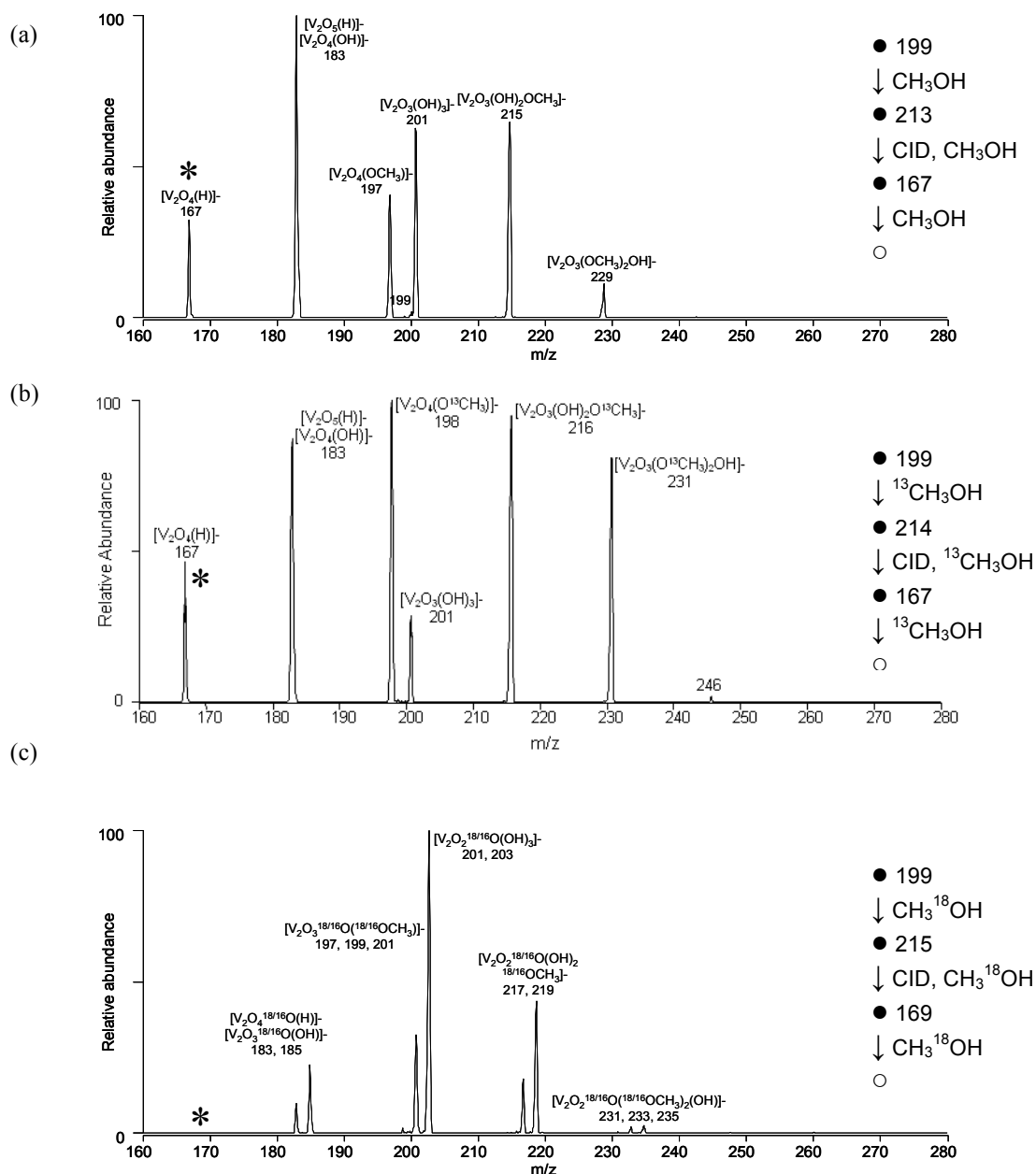


Fig. S3: Ion-molecule reaction (MS^4) of labelled $[V_2O_4(H)]^-$ (**14**) with labelled methanol: (a) $[V_2O_4(H)]^- + CH_3OH$, (b) $[V_2O_4(H)]^- + ^{13}CH_3OH$ and (c) $[V_2O_3^{18}O(H)]^- + CH_3^{18}OH$. Mass selected precursor indicated by *.

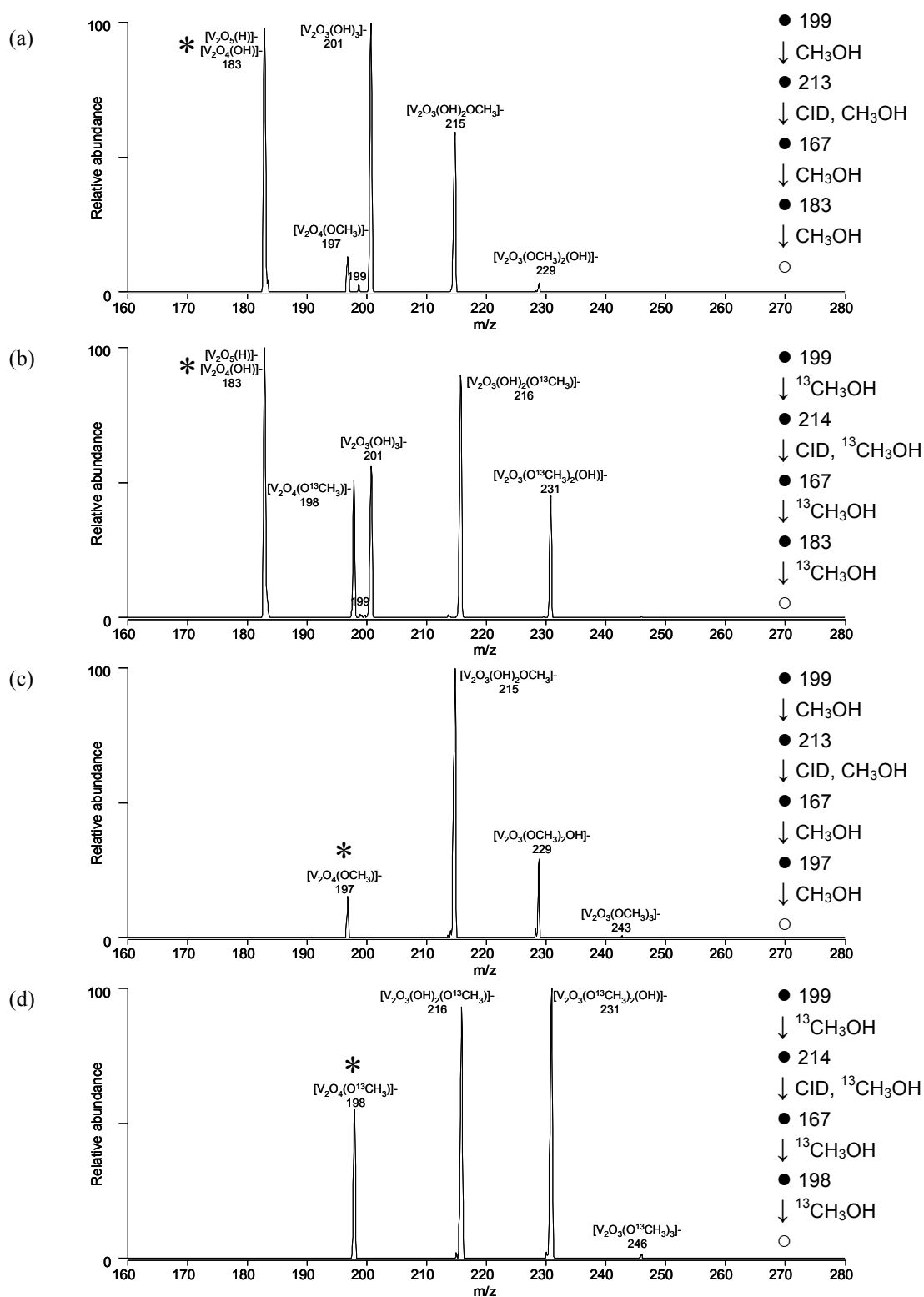


Fig. S4: Ion-molecule reaction (MS^5) of (a) $[\text{V}_2\text{O}_4(\text{OH})]^-$ (13) + CH_3OH , (b) $[\text{V}_2\text{O}_4(\text{OH})]^-$ (13) + $^{13}\text{CH}_3\text{OH}$, (c) $[\text{V}_2\text{O}_4(\text{OCH}_3)]^-$ + CH_3OH and (d) $[\text{V}_2\text{O}_4(\text{O}^{13}\text{CH}_3)]^-$ + $^{13}\text{CH}_3\text{OH}$. Mass selected precursor indicated by *.

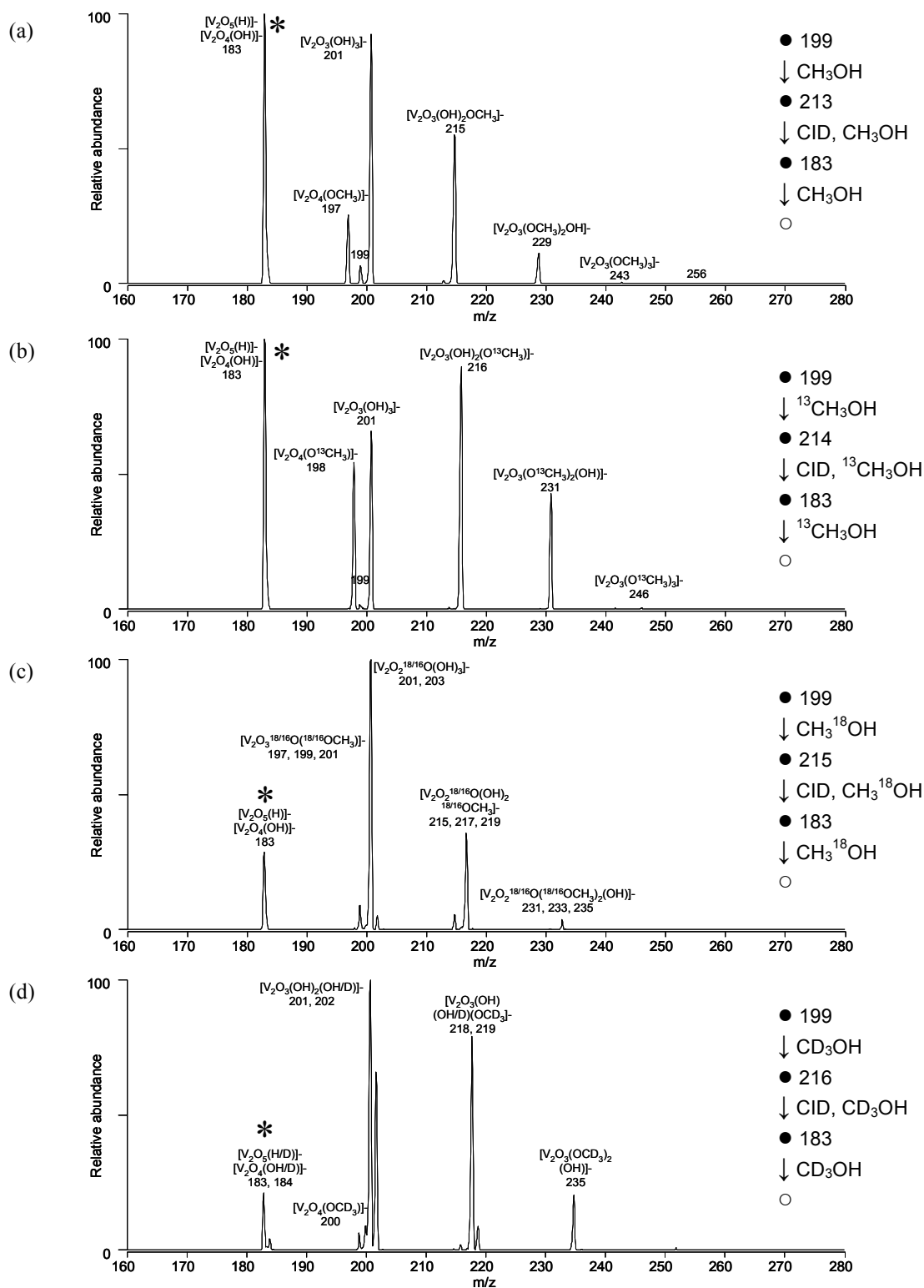


Fig. S5: Ion-molecule reaction (MS^4) of $[\text{V}_2\text{O}_4(\text{OH})]^-$ (**13**) with labelled methanol: (a) CH_3OH , (b) $^{13}\text{CH}_3\text{OH}$, (c) $\text{CH}_3^{18}\text{OH}$ and (d) CD_3OH . Mass selected precursor indicated by *.

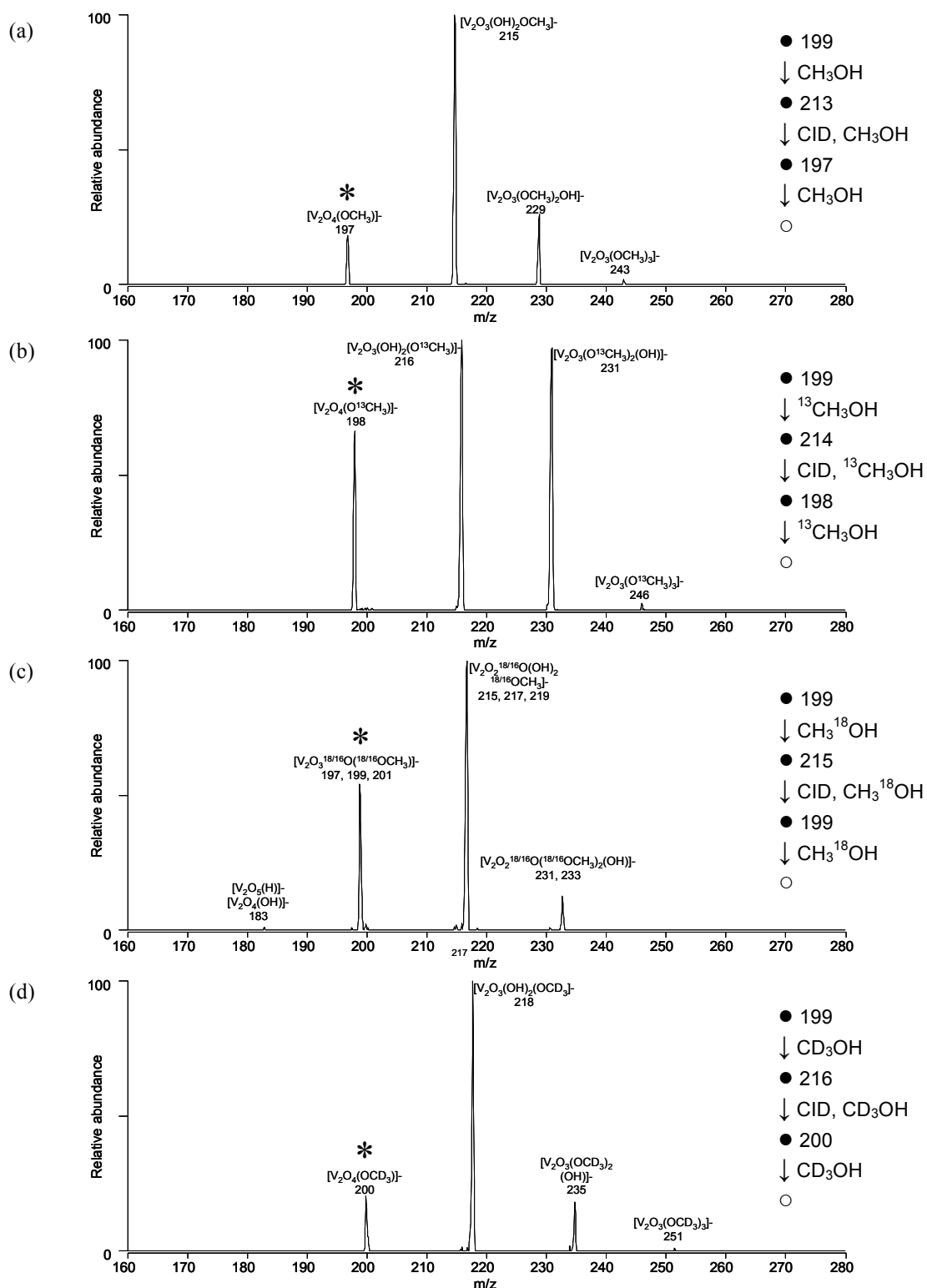


Fig. S6: Ion-molecule reaction (MS^4) of labelled $[V_2O_4(OCH_3)]^-$ with labelled methanol: (a) $[V_2O_4(OCH_3)]^- + CH_3OH$, (b) $[V_2O_4(O^{13}CH_3)]^- + ^{13}CH_3OH$, (c) $[V_2O_4(^{18}OCH_3)]^- + CH_3^{18}OH$ and (d) $[V_2O_4(OCD_3)]^- + CD_3OH$. Mass selected precursor indicated by *.

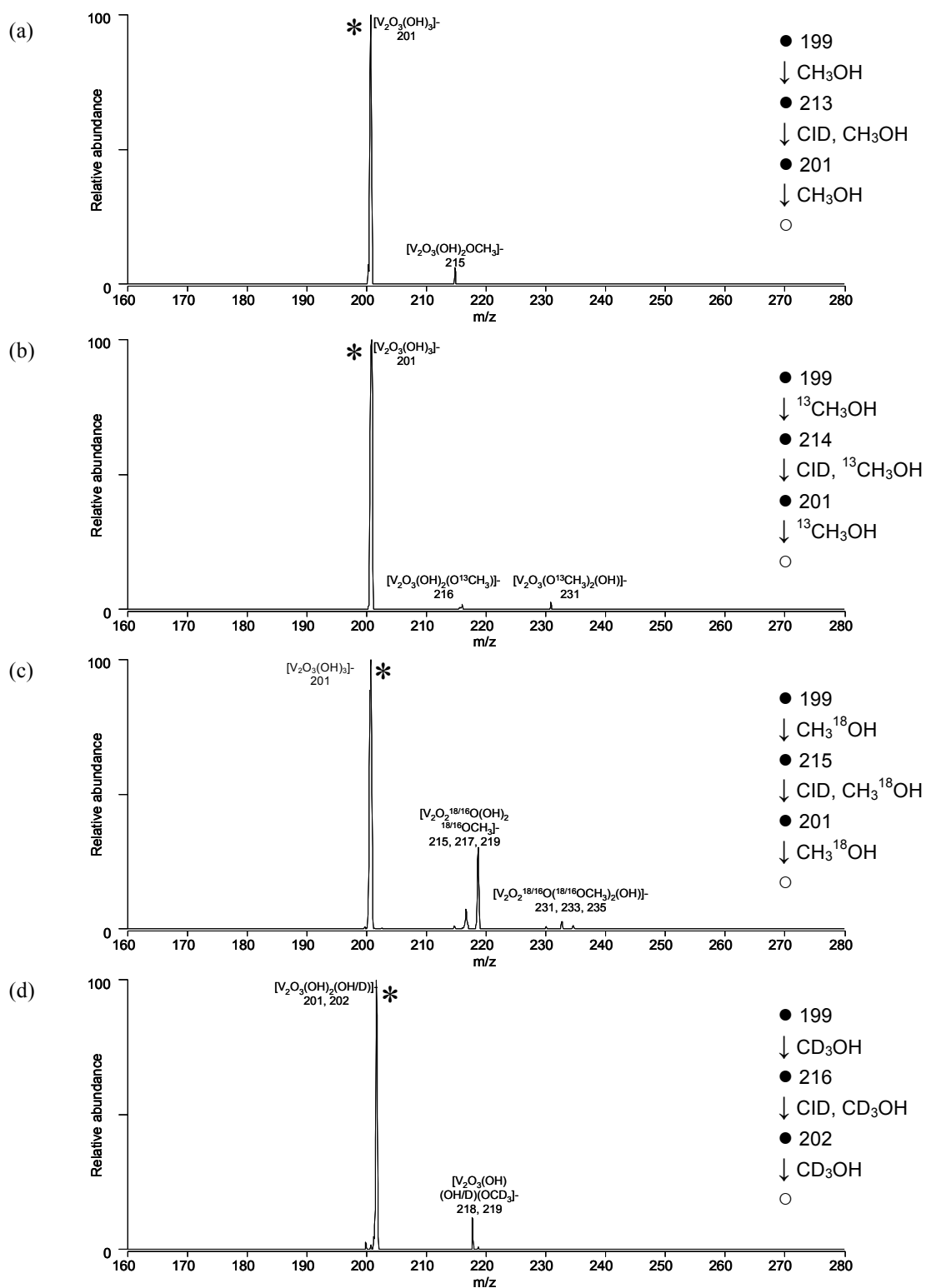


Fig. S7: Ion-molecule reaction (MS^4) of labelled $[V_2O_3(OH)_3]^-$ with labelled methanol: (a) $[V_2O_3(OH)_3]^- + CH_3OH$, (b) $^{13}CH_3OH$, (c) $[V_2O_3(OH)_3]^- + CH_3^{18}OH$ and (d) $[V_2O_3(OH)_2(OH)]^- + CD_3OH$. Mass selected precursor indicated by *.

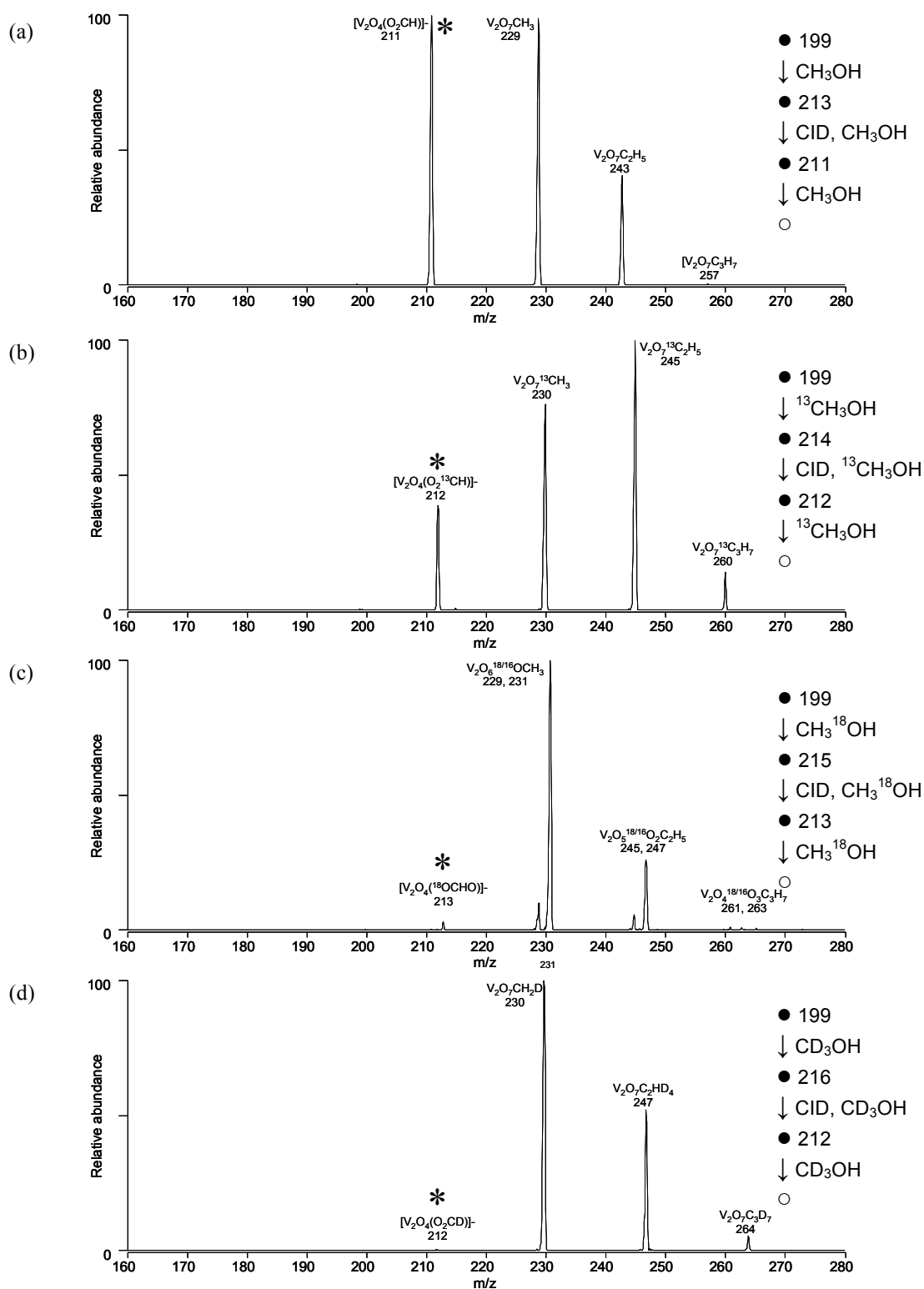


Fig. S8: Ion-molecule reaction (MS^4) of labelled $[V_2O_4(O_2CH)]^-$ (12) with labelled methanol: (a) $[V_2O_4(O_2CH)]^- + CH_3OH$, (b) $[V_2O_4(O_2^{13}CH)]^- + ^{13}CH_3OH$, (c) $[V_2O_4(^{18}OCHO)]^- + CH_3^{18}OH$ and (d) $[V_2O_4(O_2CD)]^- + CD_3OH$. Mass selected precursor indicated by *.

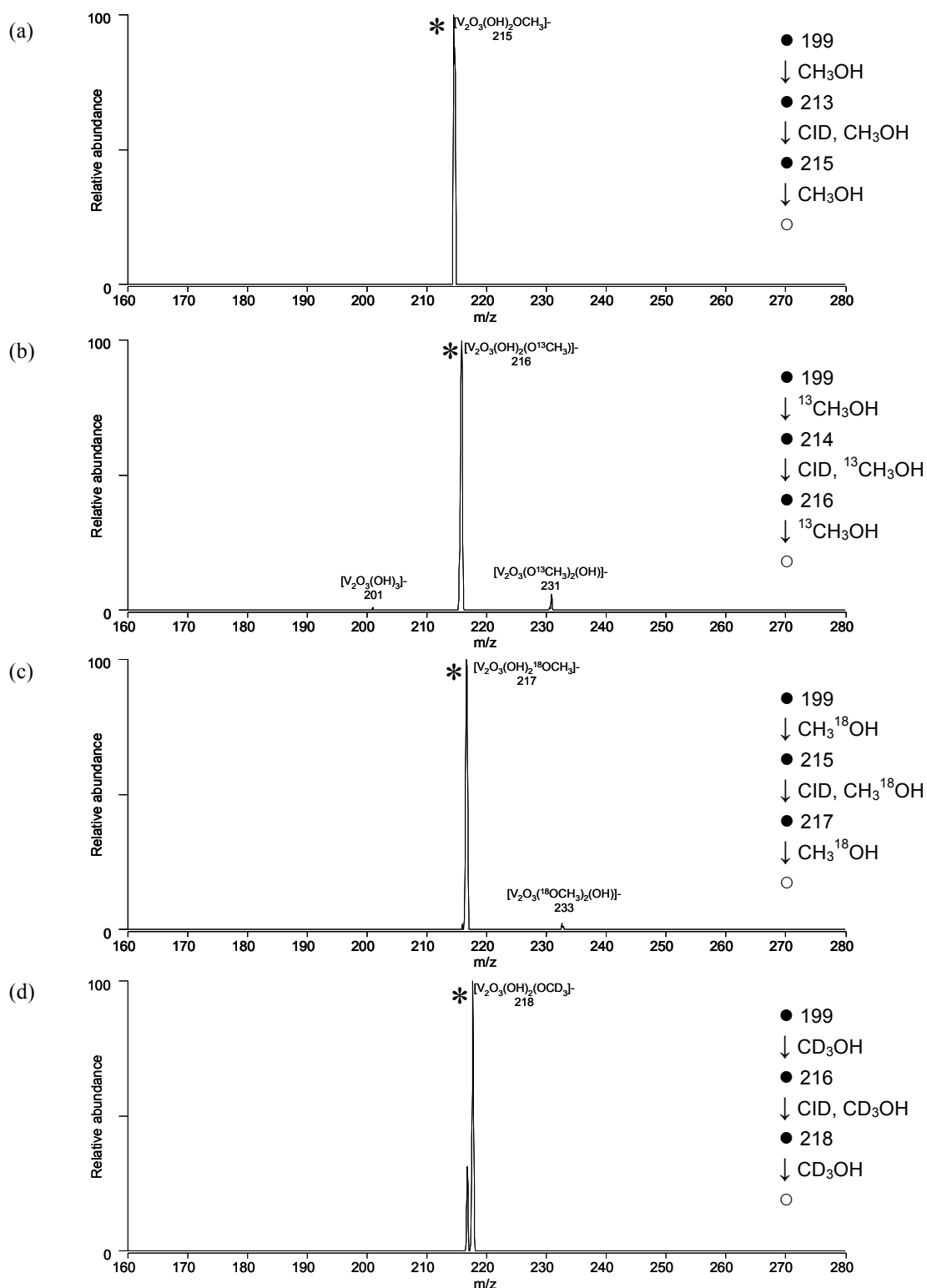


Fig. S9: Collision induced dissociation (MS^4) of labelled $[\text{V}_2\text{O}_3(\text{OH})_2\text{OCH}_3]^-$ in the presence of labelled methanol: (a) $[\text{V}_2\text{O}_3(\text{OH})_2\text{OCH}_3]^- + \text{CH}_3\text{OH}$, (b) $[\text{V}_2\text{O}_3(\text{OH})_2\text{O}^{13}\text{CH}_3]^- + ^{13}\text{CH}_3\text{OH}$, (c) $[\text{V}_2\text{O}_3(\text{OH})_2^{18}\text{OCH}_3]^- + \text{CH}_3^{18}\text{OH}$ and (d) $[\text{V}_2\text{O}_3(\text{OH})_2\text{OCD}_3]^- + \text{CD}_3\text{OH}$. Mass selected precursor indicated by *.

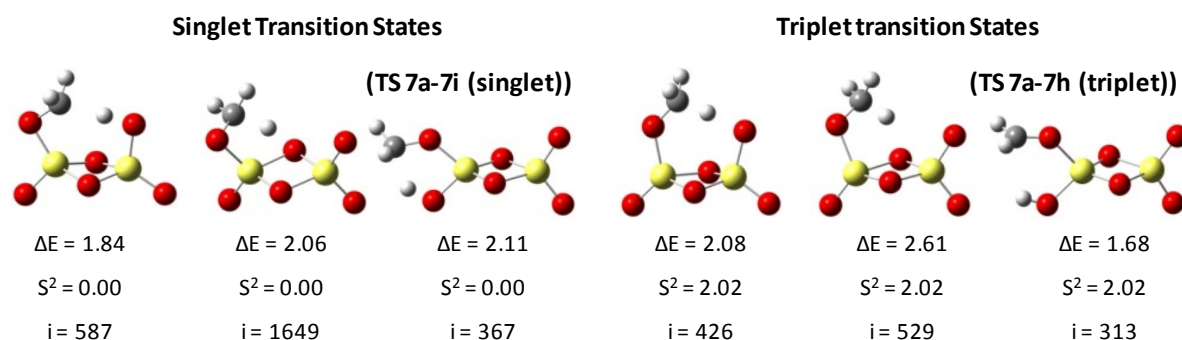
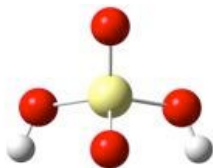


Fig. S10 A comparison of the energies for different calculated transition states on both the singlet and triplet surfaces, for the loss of formaldehyde. It is clear that the triplet TS, where the hydrogen transfers to the oxygen on the same V centre is the most favourable

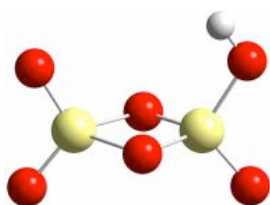
Cartesian coordinates for the
structures reported in the text

$\text{VO}_2(\text{OH})_2^-$ (1)
m/z 117
-374.140758919 Hartree ZPE -374.107979



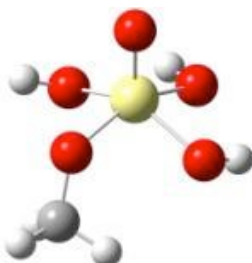
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O	8.0	-0.57116997	1.60093498	0.00000000
O	8.0	1.63801301	0.06993100	0.00000000
O	8.0	-0.57116997	-0.80191302	1.51290405
O	8.0	-0.57116997	-0.80191302	-1.51290405
H	1.0	0.11055200	-1.37424302	1.87614405
H	1.0	0.11055200	-1.37424302	-1.87614405

$\text{V}_2\text{O}_5(\text{OH})^-$ (2)
m/z 199
-595.894904717 Hartree ZPE -595.863084



V	23.0	-0.11020000	1.28359604	0.00000000
O	8.0	-0.11020000	0.04850100	1.23289204
V	23.0	0.01263000	-1.38282096	0.00000000
O	8.0	-0.11020000	0.04850100	-1.23289204
O	8.0	-1.39351702	2.22752595	0.00000000
O	8.0	1.39644206	2.29397011	0.00000000
O	8.0	1.43591404	-2.13526607	0.00000000
O	8.0	-1.21448505	-2.42041802	0.00000000
H	1.0	2.21247697	1.77966499	0.00000000

$\text{VO}(\text{OH})_3(\text{OCH}_3)^-$ (3)
m/z 149
-489.904210446 Hartree ZPE -489.818500



V	23.0	-0.32814601	0.00554000	0.20523100
O	8.0	1.47606695	-0.15581299	0.53847599
O	8.0	-0.93870401	-0.15655600	1.66175306
O	8.0	-0.04583900	1.80207205	-0.22637600
O	8.0	-0.30275401	-1.70683205	-0.64511102
O	8.0	-1.77813005	0.24039701	-1.01681805
C	6.0	2.43787789	0.04753700	-0.45244700
H	1.0	-0.71684998	2.02631402	-0.88122898
H	1.0	0.23861700	-2.29942298	-0.11281000
H	1.0	-2.00668406	-0.63987303	-1.33338201
H	1.0	2.33317590	-0.68131101	-1.27314496
H	1.0	2.34249401	1.05711496	-0.87970001
H	1.0	3.44421101	-0.06161900	-0.02076700

$\text{VO}_2(\text{OH})(\text{OCH}_3)^-$ (4)
m/z 131
-413.448746306 Hartree ZPE -413.388250



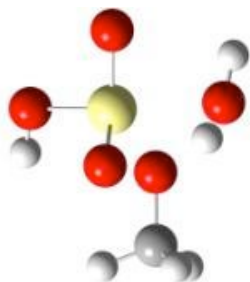
V	23.0	0.43253401	-0.10306800	0.00507600
O	8.0	1.39105403	-1.25605595	-0.60039997
O	8.0	0.35271099	-0.15247700	1.62405598
O	8.0	1.03916895	1.58153605	-0.48587701
O	8.0	-1.27619600	-0.32568699	-0.63917702
H	1.0	0.98815501	2.20680690	0.24240500
C	6.0	-2.44224691	0.11287700	-0.00710300
H	1.0	-2.40543199	-0.04901700	1.08072603
H	1.0	-2.61945510	1.18857205	-0.17777400
H	1.0	-3.31198192	-0.43158999	-0.40830600

$\text{VO}_2(\text{OH})^- (\text{CH}_3\text{OH})$ (5)
m/z 117 + H_2O
-489.927062144 Hartree ZPE -489.841178



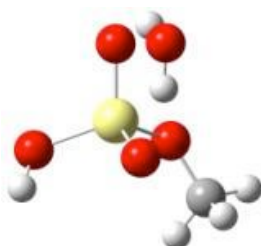
V	23.0	-0.98938602	-0.04421000	-0.09302700
O	8.0	-0.33497301	-1.35473800	-0.76947403
O	8.0	-2.04141593	0.69014603	-1.07642603
O	8.0	-1.86056101	-0.50973397	1.46501195
O	8.0	0.38360000	1.17257297	0.29309800
H	1.0	-2.68272901	-0.02856000	1.59470904
H	1.0	0.14018700	2.08131289	0.09535100
O	8.0	3.10116196	0.70033598	0.10638500
H	1.0	2.14572692	0.90337700	0.19709399
C	6.0	3.22488308	-0.70862699	0.01947700
H	1.0	4.21185303	-0.93703198	-0.39781800
H	1.0	3.15459299	-1.19001901	1.00726998
H	1.0	2.45445704	-1.14913595	-0.62261802

TS 5-6
-489.885097078 Hartree ZPE -489.802870



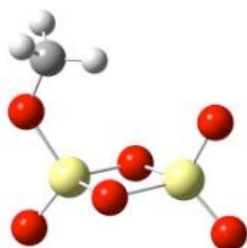
V	23.0	0.60102898	-0.09467700	0.07178200
O	8.0	2.09037709	0.39398500	-0.31618801
O	8.0	0.46801299	-0.32024500	1.65986896
O	8.0	0.52596498	-1.72811604	-0.80008000
O	8.0	-0.12503999	1.91985798	-0.20611900
H	1.0	-0.35346800	-2.10714293	-0.69918102
H	1.0	0.36781701	2.29302192	-0.94263101
H	1.0	-1.01671898	1.31709695	-0.50436699
O	8.0	-1.51988006	0.12634499	-0.60123903
C	6.0	-2.59933090	-0.23575400	0.21293201
H	1.0	-2.67294002	-1.33090305	0.31184900
H	1.0	-3.55364895	0.11399500	-0.21701300
H	1.0	-2.51419091	0.17139800	1.23281097

$\text{VO}_2(\text{OCH}_3)^- (\text{H}_2\text{O}) (6)$
m/z 131 + H_2O
-489.931699099 Hartree ZPE -489.846254



V	23.0	-0.09976800	0.35717100	-0.08906500
O	8.0	1.01784801	0.42035699	-1.26287603
O	8.0	0.50608498	-0.37560499	1.22779500
O	8.0	-0.65599000	2.05163908	0.38639399
O	8.0	-1.53914702	-0.61184198	-0.65900701
H	1.0	-0.70103002	2.18528509	1.33720696
C	6.0	-2.40136695	-1.38157105	0.12998500
H	1.0	-1.86539400	-1.88850498	0.94512498
H	1.0	-3.19499993	-0.76354402	0.58056700
H	1.0	-2.88871789	-2.14680099	-0.49256501
O	8.0	3.18845606	-0.96576202	0.14348701
H	1.0	2.47358203	-0.95444500	0.80036902
H	1.0	2.74140596	-0.50780302	-0.58844799

$\text{V}_2\text{O}_5(\text{OCH}_3)^- (7a)$
m/z 213
-635.202691529 Hartree ZPE -635.143055



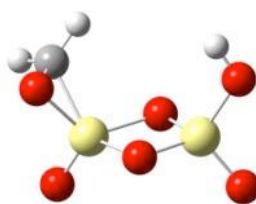
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O	8.0	-0.35164100	-0.38598800	-1.03970397
V	23.0	1.25686800	-0.61456198	-0.11981800
O	8.0	-1.93341899	-1.07338297	1.13148296
O	8.0	-1.15802896	1.68642104	0.58729100
O	8.0	-3.06789994	0.36798599	-0.96539402
O	8.0	2.47491503	-1.18212199	-1.00915694
O	8.0	0.88894600	-1.57841504	1.14450502
H	1.0	-1.07669997	-1.44511104	1.47449505
O	8.0	1.60700595	1.07234001	0.48377001
H	1.0	-0.18723400	1.72091603	0.80100298
C	6.0	2.62887692	2.01775002	0.10975200
H	1.0	3.06257510	2.46022391	1.01473904
H	1.0	3.42022800	1.52237296	-0.46514499
H	1.0	2.19013405	2.81701303	-0.50095600

$\text{V}_2\text{O}_5(\text{OH})^- (7b)$
m/z 213
-635.161829178 Hartree ZPE -635.107164



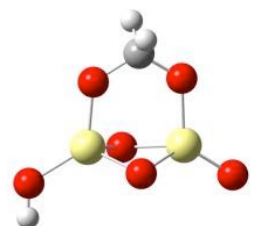
V	23.0	-1.03735399	-0.47948101	0.00001800
O	8.0	0.39515501	-0.14253600	-1.25481105
V	23.0	1.57403100	0.10038600	-0.00001100
O	8.0	0.39517000	-0.14247499	1.25481403
O	8.0	-1.59562802	-1.97430599	0.00005700
O	8.0	-2.29751611	0.89591402	-0.00000900
O	8.0	2.26285100	1.79263198	-0.00005600
O	8.0	2.77486897	-0.95704502	0.00000700
C	6.0	-3.54891896	1.26744199	-0.00001300
H	1.0	1.59079099	2.48298192	-0.00006600
H	1.0	-4.34291697	0.52300203	0.00000800
H	1.0	-3.77715492	2.33106899	-0.00003700

$V_2O_5(OCH_3)^- (7c)$
m/z 213
-635.180786944 Hartree ZPE -635.122837



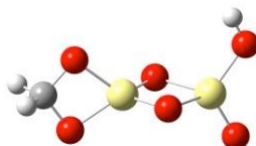
V	23.0	1.18427598	-0.29899400	0.08376400
O	8.0	-0.32188001	-0.25889501	1.25084698
V	23.0	-1.50098705	-0.02893000	-0.01461700
O	8.0	-0.25192800	-0.00459200	-1.20637906
O	8.0	1.95435202	-1.66798401	-0.14889400
O	8.0	2.35908508	0.97476900	0.70839101
O	8.0	-2.40653992	1.55283105	0.09927400
O	8.0	-2.54868197	-1.22437096	-0.17504799
C	6.0	2.31111789	1.20008695	-0.63448298
H	1.0	-1.84474695	2.33245993	0.16599400
H	1.0	1.78074598	2.09561110	-0.96975899
H	1.0	3.20639205	0.93959999	-1.20523906

$V_2O_5(OCH_3)^- (7d)$
m/z 213
-635.172031997 Hartree ZPE -635.113167



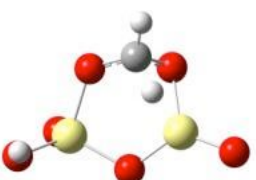
V	23.0	-0.04668200	-1.39578295	-0.00046400
O	8.0	-0.66795403	-0.07771100	1.23314703
V	23.0	-0.47544101	1.17837298	-0.00058800
O	8.0	-0.67026502	-0.07832300	-1.23340201
O	8.0	-0.66907299	-2.88168001	0.00095200
O	8.0	-1.68851995	2.54916501	0.00025100
O	8.0	1.76778805	-0.95649999	-0.00159200
O	8.0	1.31966996	1.39931405	-0.00186600
C	6.0	2.28297591	0.33852300	-0.00005600
H	1.0	2.90406203	0.47760499	0.89938599
H	1.0	2.90793395	0.47815701	-0.89669698
H	1.0	-2.63499498	2.37950206	0.00092900

$V_2O_5(OCH_3)^- (7e)$
m/z 213
-635.180108600 Hartree ZPE -635.121074



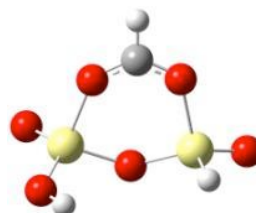
V	23.0	-0.05455900	-1.71072197	0.00000000
O	8.0	-0.01102500	-0.24966800	1.28579497
V	23.0	-0.04305000	0.91850698	0.00000000
O	8.0	-0.01102500	-0.24966800	-1.28579497
O	8.0	-1.42438996	-2.52449894	0.00000000
O	8.0	1.48752201	-2.70182395	0.00000000
H	1.0	2.35056400	-2.27746391	0.00000000
O	8.0	1.09132504	2.39964509	0.00000000
O	8.0	-1.13800097	2.43825412	0.00000000
C	6.0	-0.01102500	3.29034805	0.00000000
H	1.0	0.00268400	3.92919898	-0.90004200
H	1.0	0.00268400	3.92919898	0.90004200

TS 7d-7f
-635.145503778 Hartree ZPE -635.091580



V	23.0	1.48817599	-0.18876900	0.14864700
V	23.0	-1.63021195	-0.36082801	-0.01431300
O	8.0	2.15644193	0.09751400	1.56764102
O	8.0	-0.10070300	-1.21473396	0.21322100
O	8.0	2.60798907	-0.75711298	-1.19935298
O	8.0	0.64649898	1.46923196	-0.54595798
H	1.0	2.31819296	-0.74893802	-2.11648703
O	8.0	-3.09878302	-1.02117395	-0.07688500
H	1.0	-0.99555302	2.51493597	-1.12017298
H	1.0	-1.27240205	0.61363000	-1.41077805
O	8.0	-1.33002305	1.44289899	0.60664701
C	6.0	-0.63912803	1.68801999	-0.49412400

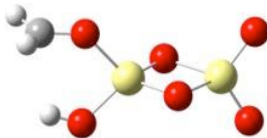
$V_2O_5(OCH_3)^- (7f)$
m/z 213
-635.175502349 Hartree ZPE -635.121716



V	23.0	1.75492597	-0.44985700	0.16554400
V	23.0	-1.54237604	-0.26580200	-0.13268200
O	8.0	0.13387400	-1.01886201	-0.29491201
O	8.0	-2.42689800	-0.30071700	-1.46143794
O	8.0	3.14420509	-0.88646901	-0.51309001
O	8.0	1.41980100	1.55216897	0.11343000
O	8.0	-2.33249807	-0.75607902	1.45112503
O	8.0	-0.84449703	1.62964797	0.04993400
C	6.0	0.31204399	2.13715005	0.06145100
H	1.0	0.34621599	3.23746991	0.03262700
H	1.0	1.95678794	-0.53999501	1.82173896
H	1.0	-1.81581998	-0.81774497	2.26073790

TS 7a-7g

-635.135454498 Hartree
ZPE -635.081281

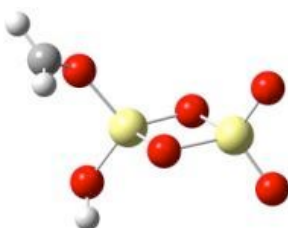


V	23.0	-0.88667399	0.21192600	0.00000200
O	8.0	0.33754000	0.05500100	1.23509097
V	23.0	1.76625395	-0.10794200	0.00001300
O	8.0	0.33751401	0.05549900	-1.23508501
O	8.0	-1.98288298	1.68124294	-0.00001300
O	8.0	-2.36555099	-0.97713000	-0.00003200
O	8.0	2.50425911	-1.53888500	-0.00026400
O	8.0	2.81376195	1.11427999	0.00023200
C	6.0	-3.67087293	-0.87351799	0.00011300
H	1.0	-2.93730688	1.53309298	-0.00092400
H	1.0	-4.21261597	-0.90287697	-0.94462401
H	1.0	-4.21230078	-0.90079600	0.94509900

Triplet $[V_2O_4(OH)(OCH_2)]^-$
(7g)

m/z 213

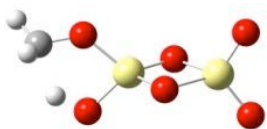
-635.144301736 Hartree
ZPE -635.090051



V	23.0	-0.97260302	0.38857099	0.16632800
O	8.0	0.13891099	-0.10655200	-1.13485706
V	23.0	1.64814305	-0.18401700	-0.03398800
O	8.0	0.37810701	0.32130101	1.27627695
O	8.0	-1.75033200	2.02099991	-0.13321200
O	8.0	-2.36582589	-0.81806803	0.39974901
O	8.0	2.28553605	-1.65329003	0.15009899
O	8.0	2.78075910	0.92101902	-0.34495601
C	6.0	-3.14255500	-1.50524998	-0.39685401
H	1.0	-1.52902198	2.47641206	-0.95177501
H	1.0	-2.93095994	-1.56443906	-1.46218204
H	1.0	-3.95934105	-2.06849790	0.04644700

TS 7a-7h

-635.120549113 Hartree
ZPE -635.065319

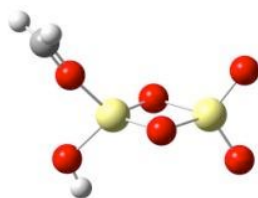


V	23.0	0.89528501	0.14448200	-0.06224600
O	8.0	-0.34280401	0.06496000	-1.26555002
V	23.0	-1.76024604	-0.07782400	0.02353800
O	8.0	-0.28901801	0.07599000	1.21806204
O	8.0	2.02740908	1.47474205	-0.00011700
O	8.0	2.31031895	-0.89284497	-0.16638100
O	8.0	-2.50611591	-1.50049305	0.04104200
O	8.0	-2.80145192	1.14423299	0.05048200
C	6.0	3.59289789	-0.62170100	0.17799400
H	1.0	3.00107908	1.05957997	0.04427500
H	1.0	3.81673408	-0.72016501	1.24367595
H	1.0	4.33220720	-1.07504106	-0.48592401

Singlet $[V_2O_4(OH)(OCH_2)]^-$
(7h)

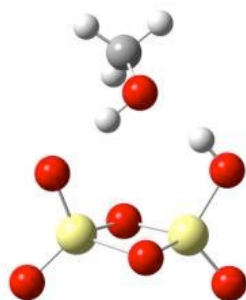
m/z 213

-635.142762377 Hartree
ZPE -635.069103



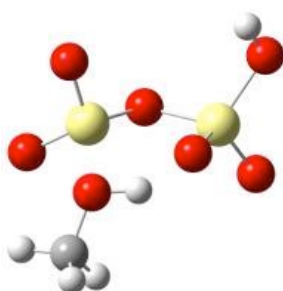
V	23.0	-0.93153101	0.35582900	-0.01457100
O	8.0	0.32091299	0.27771401	1.21186996
V	23.0	1.68727899	-0.19621900	0.00914300
O	8.0	0.22211300	-0.09903000	-1.21605599
O	8.0	-1.80673897	1.99219704	0.02206800
O	8.0	-2.42265701	-0.64524800	-0.01844000
O	8.0	2.31278896	-1.66932404	0.18997200
O	8.0	2.82007098	0.93344003	-0.18417700
C	6.0	-3.37463903	-1.49548995	0.01437000
H	1.0	-1.21913397	2.74548602	-0.10600200
H	1.0	-4.02501297	-1.53101695	0.88520199
H	1.0	-3.46213508	-2.23055696	-0.78247499

$V_2O_5(OH)^- (CH_3OH) (8)$
m/z 199 + CH_3OH
-711.683294647 Hartree ZPE -711.597245



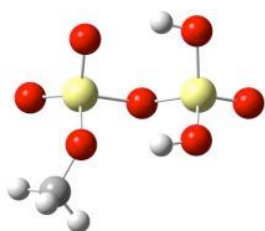
V	23.0	-0.88654602	-1.18118501	0.01379300
O	8.0	-1.05383801	0.11606100	-1.16559398
V	23.0	-0.39204001	1.42492902	-0.01354000
O	8.0	-0.47265700	0.03049600	1.22524595
O	8.0	-2.20973301	-2.01870608	0.30300099
O	8.0	0.49162400	-2.24829602	-0.34878600
O	8.0	1.14937699	1.84008396	-0.36068600
O	8.0	-1.33258498	2.69488811	0.26086399
H	1.0	1.31719303	-1.73333895	-0.50560498
O	8.0	2.66392994	-0.45014501	-0.56336898
H	1.0	2.17656302	0.40727001	-0.59373802
C	6.0	3.48325491	-0.44012100	0.59682798
H	1.0	2.89162993	-0.30258900	1.50967395
H	1.0	4.23993397	0.35286099	0.54557800
H	1.0	3.99368596	-1.40466106	0.65189201

TS 8-9
-711.667223736 Hartree ZPE -711.582606



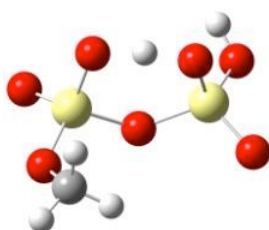
V	23.0	1.05927205	-0.70153397	0.11780200
O	8.0	-0.56658602	-0.83120501	0.96604103
V	23.0	-1.67376995	0.24597301	0.09274600
O	8.0	-0.53578401	0.90299600	-0.96257401
O	8.0	2.20664406	-0.77091902	1.24314106
O	8.0	1.25415504	-1.90589702	-0.92041498
O	8.0	-2.96966696	-0.68442899	-0.79084599
O	8.0	-2.35961103	1.33750498	1.04241502
H	1.0	-2.61813402	-1.27057099	-1.47073805
H	1.0	0.98085701	1.32147300	-1.09901202
O	8.0	1.88610101	0.97830600	-0.82365298
C	6.0	2.65042496	1.94574797	-0.09536000
H	1.0	3.44940710	1.41015506	0.41302100
H	1.0	3.06616497	2.67697811	-0.79511702
H	1.0	2.03059292	2.45451808	0.64852899

$V_2O_4(OH)_2(OCH_3)^- (9)$
m/z 231
-711.695181484 Hartree ZPE -711.337473



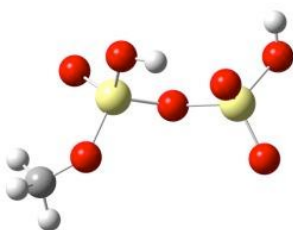
V	23.0	-1.72909796	0.16079600	-0.12561600
O	8.0	-0.35164100	-0.38598800	-1.03970397
V	23.0	1.25686800	-0.61456198	-0.11981800
O	8.0	-1.93341899	-1.07338297	1.13148296
O	8.0	-1.15802896	1.68642104	0.58729100
O	8.0	-3.06789994	0.36798599	-0.96539402
O	8.0	2.47491503	-1.18212199	-1.00915694
O	8.0	0.88894600	-1.57841504	1.14450502
H	1.0	-1.07669997	-1.44511104	1.47449505
O	8.0	1.60700595	1.07234001	0.48377001
H	1.0	-0.18723400	1.72091603	0.80100298
C	6.0	2.62887692	2.01775002	0.10975200
H	1.0	3.06257510	2.46022391	1.01473904
H	1.0	3.42022800	1.52237296	-0.46514499
H	1.0	2.19013405	2.81701303	-0.50095600

TS 9-10
-711.685683212 Hartree ZPE -711.606489



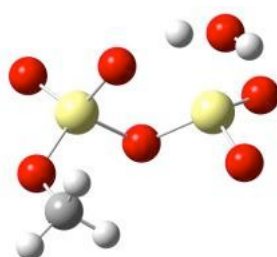
V	23.0	1.38523901	-0.57141501	-0.09789200
O	8.0	-0.19819000	-0.21522699	-0.86217803
V	23.0	-1.75697601	0.20821500	-0.09533700
O	8.0	0.95391601	-0.55084199	1.54257298
O	8.0	2.01962900	-1.96925604	-0.53610998
O	8.0	2.55526209	0.75114202	-0.45223400
O	8.0	-2.96793509	-1.13522899	-0.27461001
O	8.0	-2.39559603	1.54975295	-0.67202097
C	6.0	2.43965912	2.08125401	0.00508100
H	1.0	2.36632490	2.12015390	1.09945500
H	1.0	3.33025599	2.63972211	-0.30876401
H	1.0	1.55384195	2.57330203	-0.41648999
O	8.0	-1.26836598	0.38511801	1.51886106
H	1.0	-0.15977800	-0.07071800	1.67744899
H	1.0	-2.76840210	-1.92006695	0.24788000

$V_2O_4(OH)_2(OCH_3)^- (10)$
m/z 231
-711.695827862 Hartree ZPE -711.612301



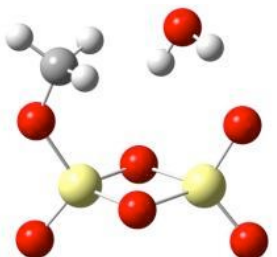
V	23.0	-1.88241196	0.28632900	-0.02814700
O	8.0	-1.67181695	-0.22303601	1.50540102
V	23.0	1.28757095	-0.44161001	-0.11039500
O	8.0	-0.20477600	0.03815300	-0.82324803
O	8.0	-3.12751698	-0.74774897	-0.87924403
O	8.0	-2.32711196	1.82618296	-0.07903600
O	8.0	2.25766397	0.98236799	0.34536299
O	8.0	2.17193699	-1.30574906	-1.10713506
C	6.0	3.54767990	1.41491795	-0.00214400
H	1.0	4.02980900	0.71707201	-0.69792700
H	1.0	4.16626215	1.49797499	0.90077102
H	1.0	3.49122405	2.40407109	-0.47373399
O	8.0	0.88828999	-1.41817105	1.32457101
H	1.0	0.02799000	-1.11754000	1.69471204
H	1.0	-3.21337295	-1.63561296	-0.51786798

TS 10-11
-711.666263300 Hartree ZPE -711.582165



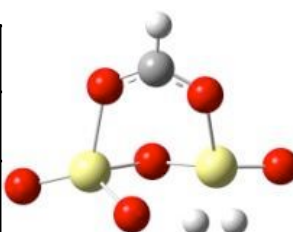
V	23.0	-1.30898905	-0.57061499	-0.03835500
O	8.0	-0.01111300	-0.27545899	-1.21845603
V	23.0	1.51624203	0.11089900	-0.28272599
O	8.0	-2.00619507	-2.00349498	-0.19909200
O	8.0	-0.38467801	-0.41775101	1.36536598
O	8.0	-2.56597209	0.72587198	-0.13666500
O	8.0	2.74521804	-0.61746901	-1.00356901
O	8.0	1.78356600	1.69731700	-0.25665000
C	6.0	-2.32227206	2.09553194	0.09332300
H	1.0	-1.52269995	2.48024011	-0.55207503
H	1.0	-3.24153304	2.65781212	-0.11618000
H	1.0	-2.03263402	2.27762103	1.13722801
O	8.0	2.01424408	-0.30210301	1.73417497
H	1.0	2.33759093	0.52310503	2.11182094
H	1.0	1.02554703	-0.39379600	1.96324396

$V_2O_5(OH)^- (CH_3OH) (11)$
m/z 213 + H_2O
-711.678907975 Hartree ZPE -711.594288



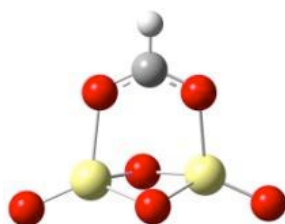
V	23.0	1.46363497	-0.32875401	-0.20211200
O	8.0	0.17510401	-0.07139000	1.14696801
V	23.0	-1.15772498	-0.68900597	0.16882899
O	8.0	-0.02731900	-1.02535701	-1.12253904
O	8.0	2.03319192	1.08332598	-0.75354099
O	8.0	2.63691092	-1.37455106	0.11595500
O	8.0	-1.89406598	-1.96751201	0.76882201
O	8.0	-2.35366011	0.56097299	-0.27209401
C	6.0	-2.11044693	1.79745197	-0.92723799
H	1.0	-3.07142496	2.30525088	-1.06541002
H	1.0	-1.65247202	1.63149500	-1.90929306
H	1.0	-1.44626904	2.43645406	-0.33638600
O	8.0	0.69820601	2.97698212	1.08664095
H	1.0	0.39324301	2.16148305	1.50685406
H	1.0	1.25672197	2.62933803	0.37146500

TS 7f-12a
m/z 213
-635.136746043 Hartree ZPE -635.084651



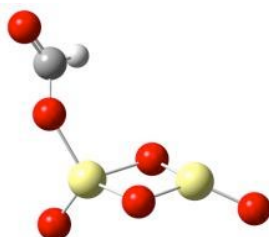
V	23.0	1.42995405	-0.42927700	0.01056600
V	23.0	-1.43068302	-0.30694801	-0.00099300
O	8.0	0.10244600	-0.79934198	-1.05492401
O	8.0	-2.90609598	-0.82172799	-0.42855600
O	8.0	2.93472290	-0.79550898	-0.41817001
O	8.0	1.17844200	1.57185304	0.20948300
O	8.0	-0.67303801	-0.60086501	1.52174306
O	8.0	-1.02893698	1.69889605	-0.27305701
C	6.0	0.10491600	2.18853092	-0.05114700
H	1.0	0.18147600	3.28615189	-0.07878700
H	1.0	1.60609102	-0.78541303	1.85823298
H	1.0	0.73938298	-0.72519398	1.85510504

$V_2O_4(OCHO)^- (12a)$
m/z 211
-633.981136900 Hartree ZPE -633.943068



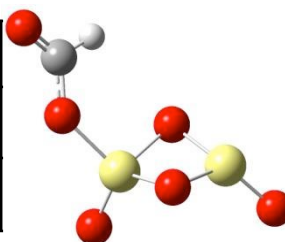
V	23.0	1.32854903	-0.36055300	-0.06104700
O	8.0	-0.04778400	-0.64558399	1.25334406
V	23.0	-1.32854903	-0.36055300	0.06104700
O	8.0	0.04778400	-0.64558500	-1.25334406
O	8.0	2.78529310	-1.05368304	0.06164700
O	8.0	-2.78529310	-1.05368304	-0.06164600
O	8.0	1.12778103	1.68680704	0.10761000
C	6.0	0.00000000	2.24050498	0.00000000
H	1.0	-0.00000100	3.34177208	0.00000200
O	8.0	-1.12778103	1.68680704	-0.10761100

$V_2O_4(OCHO)^- (12b)$
m/z 211
-633.964270907 Hartree ZPE -633.927854



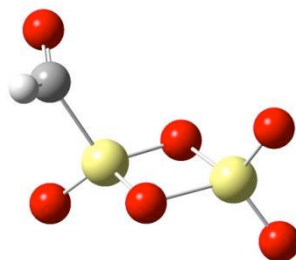
V	23.0	0.06438300	-1.19233799	0.00000000
O	8.0	-0.55384600	-0.15609200	1.37500405
V	23.0	-0.53428400	1.01818395	0.00000000
O	8.0	-0.55384600	-0.15609200	-1.37500405
O	8.0	-0.55384600	-2.68926692	0.00000000
O	8.0	-2.10089993	1.98385406	0.00000000
O	8.0	1.86304903	-0.79494601	0.00000000
O	8.0	1.20537198	1.51283395	0.00000000
C	6.0	2.26669502	0.55375999	0.00000000
H	1.0	2.87231207	0.73877901	0.89978898
H	1.0	2.87231207	0.73877901	-0.89978898
H	1.0	-2.98492002	1.60310698	0.00000000

$V_2O_4(OCHO)^- (12c)$
m/z 211
-633.940882831 Hartree ZPE -633.903919



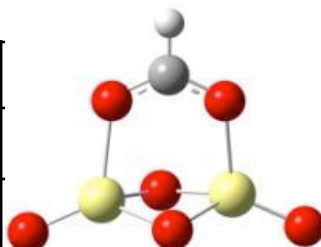
V	23.0	0.25839999	0.72199202	0.02621900
O	8.0	-0.34835801	-0.57147503	-1.11524105
O	8.0	-0.72311902	0.06209200	1.40549302
C	6.0	2.82827210	-0.73357302	-0.22783600
O	8.0	3.94685602	-0.98273998	0.16873100
O	8.0	-0.02475700	2.22951508	-0.39418799
H	1.0	2.32576704	-1.36552095	-0.98505503
V	23.0	-1.69169295	-0.69745803	0.08015800
O	8.0	-3.23545003	-0.37277201	-0.23504600
O	8.0	2.09362006	0.28571299	0.15842600

$V_2O_5(CHO)^- (12d)$
m/z 211
Hartree -633.939386804 ZPE -633.904225

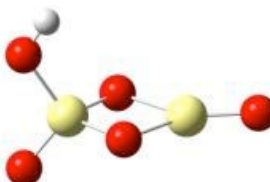


V	23.0	-0.38939899	-1.21504700	-0.27004400
O	8.0	-0.60574698	0.10468500	0.88943899
V	23.0	-0.10282600	1.56343198	0.02224500
O	8.0	0.11352200	0.24370000	-1.13723803
O	8.0	-1.68606198	-2.00017500	-0.78408402
O	8.0	1.26306605	2.23995805	0.55340499
O	8.0	-1.22247696	2.67586088	-0.29881501
C	6.0	0.88872600	-2.34981394	0.10572700
H	1.0	1.16577494	-2.25216293	1.16577804
O	8.0	0.49070799	-3.51394200	-0.11538100

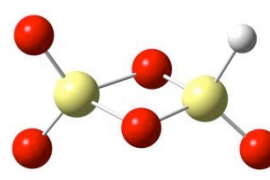
$V_2O_4(OCHO)^- (12e)$
m/z 211
-633.981136900 Hartree ZPE -633.943068

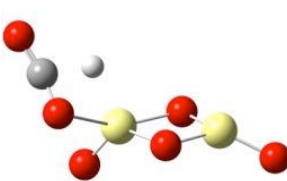


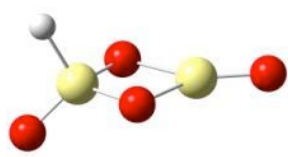
V	23.0	1.32854903	-0.36055300	-0.06104700
O	8.0	-0.04778400	-0.64558399	1.25334406
V	23.0	-1.32854903	-0.36055300	0.06104700
O	8.0	0.04778400	-0.64558500	-1.25334406
O	8.0	2.78529310	-1.05368304	0.06164700
O	8.0	-2.78529310	-1.05368304	-0.06164600
O	8.0	1.12778103	1.68680704	0.10761000
C	6.0	0.00000000	2.24050498	0.00000000
H	1.0	-0.00000100	3.34177208	0.00000200
O	8.0	-1.12778103	1.68680704	-0.10761100

Triplet $[\text{V}_2\text{O}_4(\text{OH})]^-$ (13a)		V	23.0	0.68632901	0.91874200	0.00000000
m/z 183		V	23.0	-0.82748097	-1.31754100	0.00000000
-520.583825595 Hartree ZPE -520.556693		O	8.0	2.28738809	0.98285502	0.00000000
		O	8.0	0.01273700	2.62273407	0.00000000
		O	8.0	0.01273700	-0.08331900	1.25108397
		O	8.0	0.01273700	-0.08331900	-1.25108397
		O	8.0	-1.80112600	-2.62563491	0.00000000
		H	1.0	-0.94931197	2.66586399	0.00000000

Singlet [V ₂ O ₄ (OH)] ⁻ (13b)		V	23.0	0.15152401	1.11065304	0.00000000
<i>m/z</i> 183		O	8.0	0.15152401	-0.12949400	1.26303005
-520.562825035 Hartree ZPE -520.535662		V	23.0	0.01258500	-1.49656498	0.00000000
		O	8.0	0.15152401	-0.12949400	-1.26303005
		O	8.0	1.45961499	2.02640605	0.00000000
		O	8.0	-1.35667801	2.13585305	0.00000000
		O	8.0	-0.60592401	-2.99701095	0.00000000
		H	1.0	-2.17497206	1.62588596	0.00000000

Singlet [V ₂ O ₄ (OH)] ⁻ (13c)		V	23.0	-0.05852500	1.19357800	0.00000000
<i>m/z</i> 183		O	8.0	-0.05852500	-0.25733301	1.23976398
-520.579556573 Hartree ZPE -520.554538		V	23.0	-0.13148101	-1.46588504	0.00000000
		O	8.0	-0.05852500	-0.25733301	-1.23976398
		O	8.0	1.27140200	2.09240890	0.00000000
		O	8.0	-1.38386095	2.10038090	0.00000000
		O	8.0	0.97469002	-2.61842704	0.00000000
	H	1.0	-1.59132302	-2.21451592	0.00000000	

TS 12b-14		V	23.0	-0.49769500	0.57883102	-0.01525100
		O	8.0	0.62454498	-0.71646500	-0.92506498
		O	8.0	1.09103096	0.75665599	1.08800197
		V	23.0	1.98275006	-0.42702201	0.16137300
		O	8.0	3.57894206	-0.45583600	-0.15436400
		O	8.0	-0.94213802	2.00003195	-0.58027101
		O	8.0	-2.34135294	-0.64572901	-0.90982401
		C	6.0	-2.98854709	-0.68813801	0.07749900
-633.880036 -635.049542		O	8.0	-3.84162498	-0.87926602	0.84740800
		H	1.0	-1.58019900	0.16207100	1.24711502

Triplet [V ₂ O ₄ (O ₂ CH)] ⁻ (14)		V	23.0	0.11898800	-1.34885502	0.00000000
<i>m/z</i> 167		O	8.0	0.08079900	0.15169001	1.26057994
-445.271915211 Hartree ZPE - 445.251497		O	8.0	0.08079900	0.15169001	-1.26057994
		V	23.0	0.08079900	1.33560002	0.00000000
		O	8.0	0.16070400	-2.97596693	0.00000000
		O	8.0	-1.08590603	2.44135594	0.00000000
		H	1.0	1.51372194	2.15471697	0.00000000