Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Correlation between the acid-base properties of the La_2O_3 catalyst and its methane reactivity

Changqing Chu,[a,b] Yonghui Zhao,[a] Shenggang Li,[a,c,*] and Yuhan Sun[a,c]

[a]CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, 100 Haike Road, Shanghai 201210, China.

[b]University of Chinese Academy of Sciences, 19 Yuquan Road, Shijingshan District, Beijing 100049, China

[c]School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China

This supplementary information is divided into three sections, briefly summarized below.

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Section 2: additional figures:

Figure S1. Structures of Protonated Clusters and Clusters with the F^- Anion Attached.

Figure S2. Structures of Clusters upon CO_2 Chemisorption.

Figure S3. Potential Energy Surfaces for CH_4 Activation by La_4O_6 (C_{2v}) and (C_{2h}).

Section 3: additional tables for Cartesian coordinates of structures in **Figures S1-S3**.

Section 1.

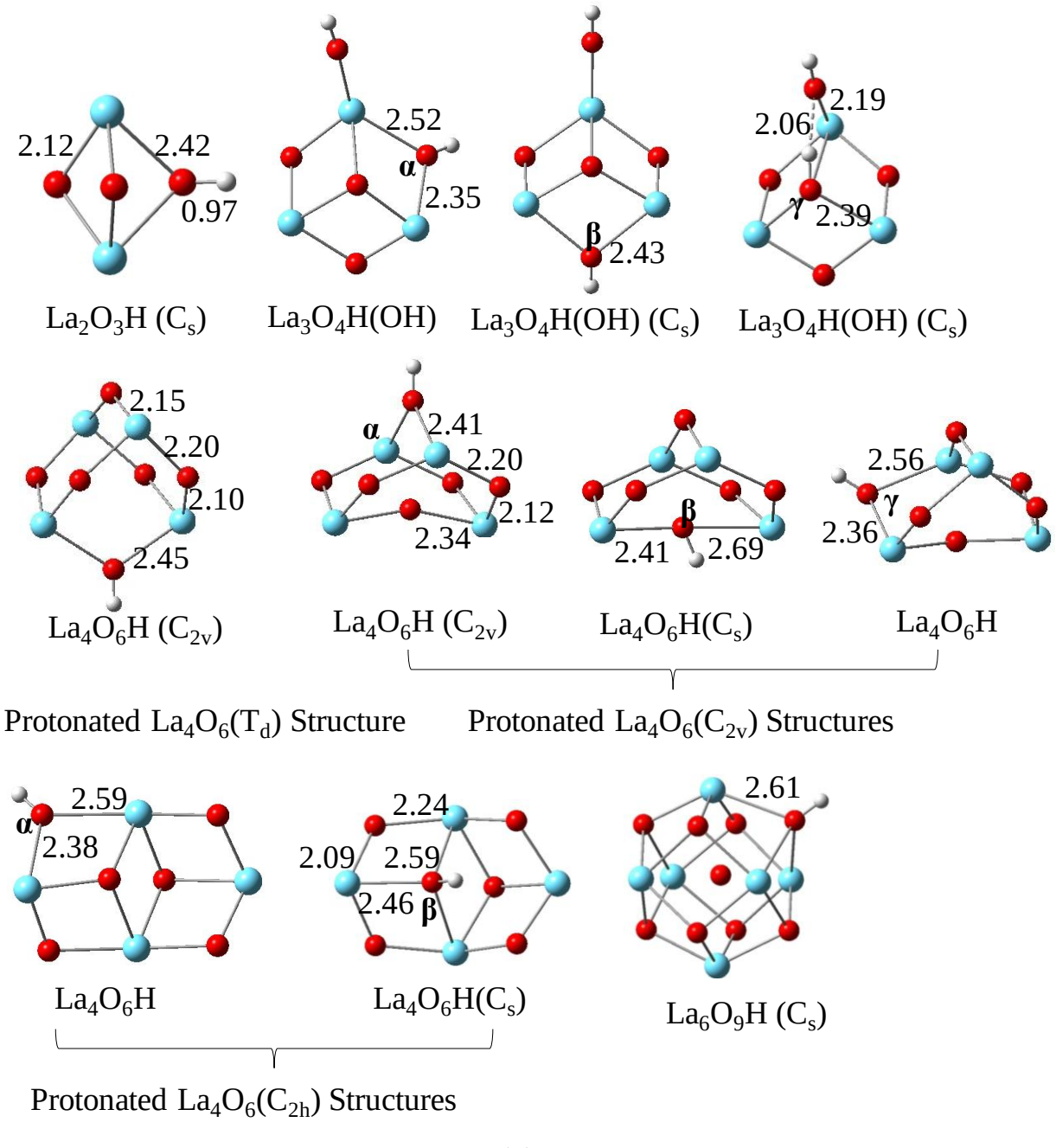
Complete lists of references 41 and 42

Ref. 41: Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

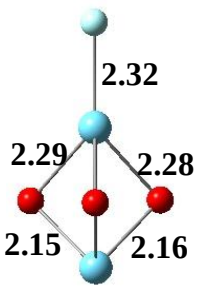
Ref. 42: MOLPRO, version 2012.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, see http://www.molpro.net.

Section 2.

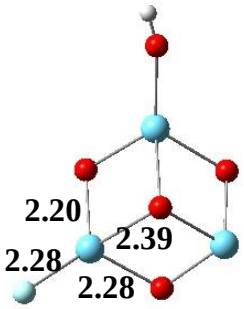
Figure S1. Structures of (a) the Protonated Clusters and (b) Clusters with the F^- Anion Attached with Selected B3LYP/aVDZ Bond Distances Shown in Å.



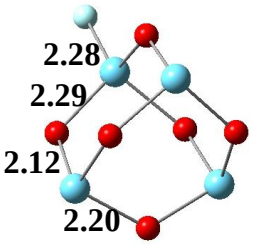
(a)



La_2O_3F (C_s)

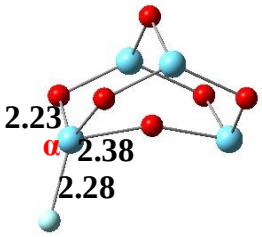


$La_3O_4(OH)F$

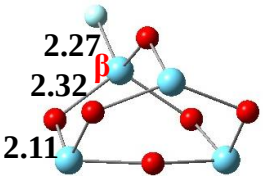


La_4O_6F (C_{3v})

F^- Binding $La_4O_6(T_d)$ Structure

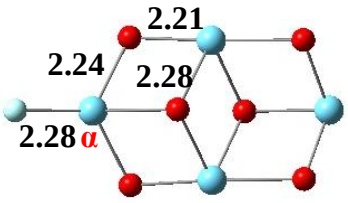


$La_4O_6F(C_s)$

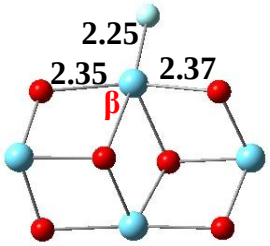


$La_4O_6F(C_s)$

F^- Binding $La_4O_6(C_{2v})$ Structures

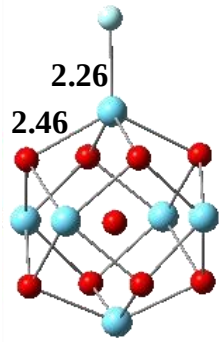


$La_4O_6F(C_S)$



La_4O_6F

F^- Binding $La_4O_6(C_{2h})$ Structures



La_6O_9F (C_{4v})

(b)

Figure S2. Structures of Clusters upon CO_2 Chemisorption with Selected B3LYP/aVDZ Bond Distances Shown in Å.

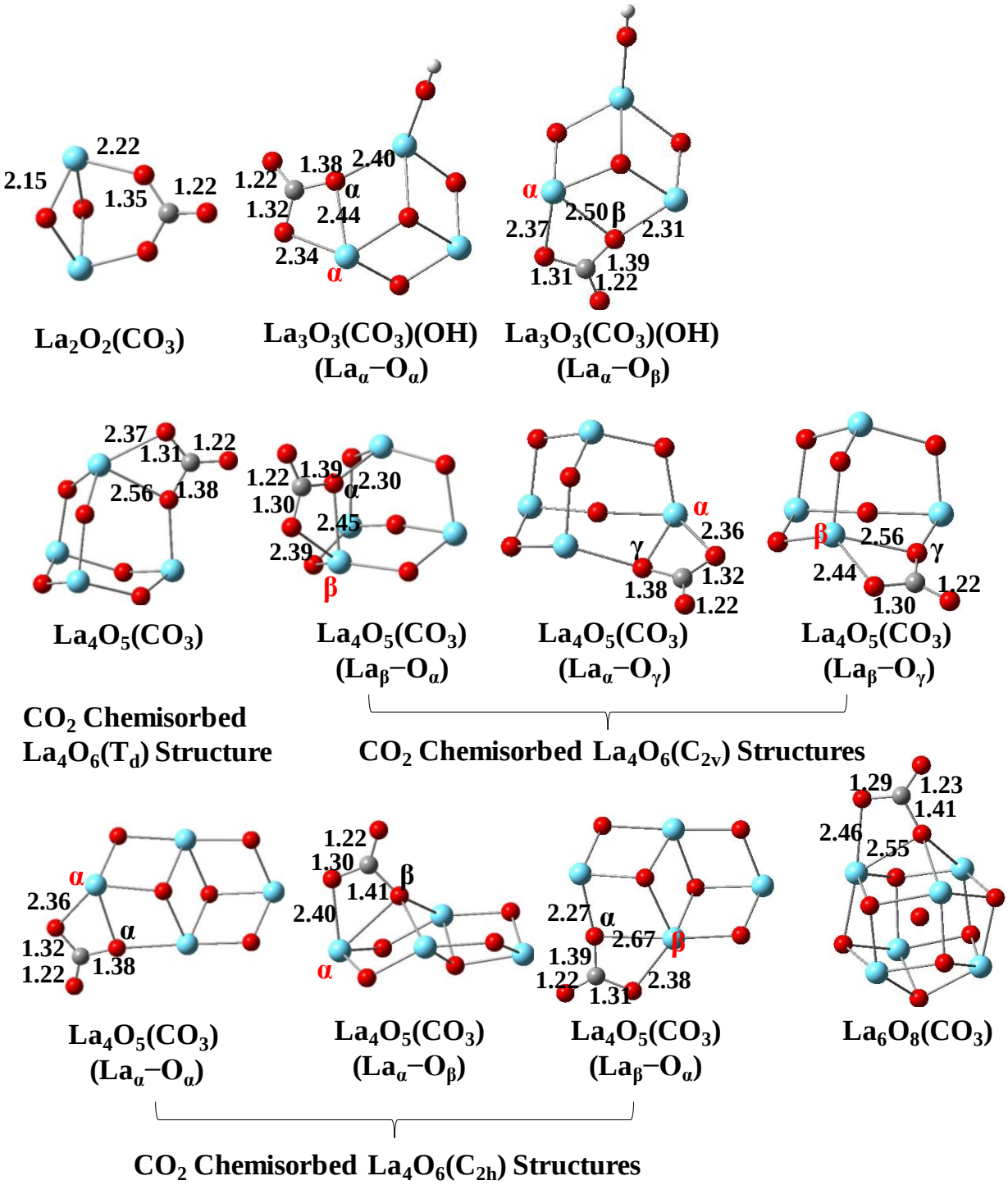
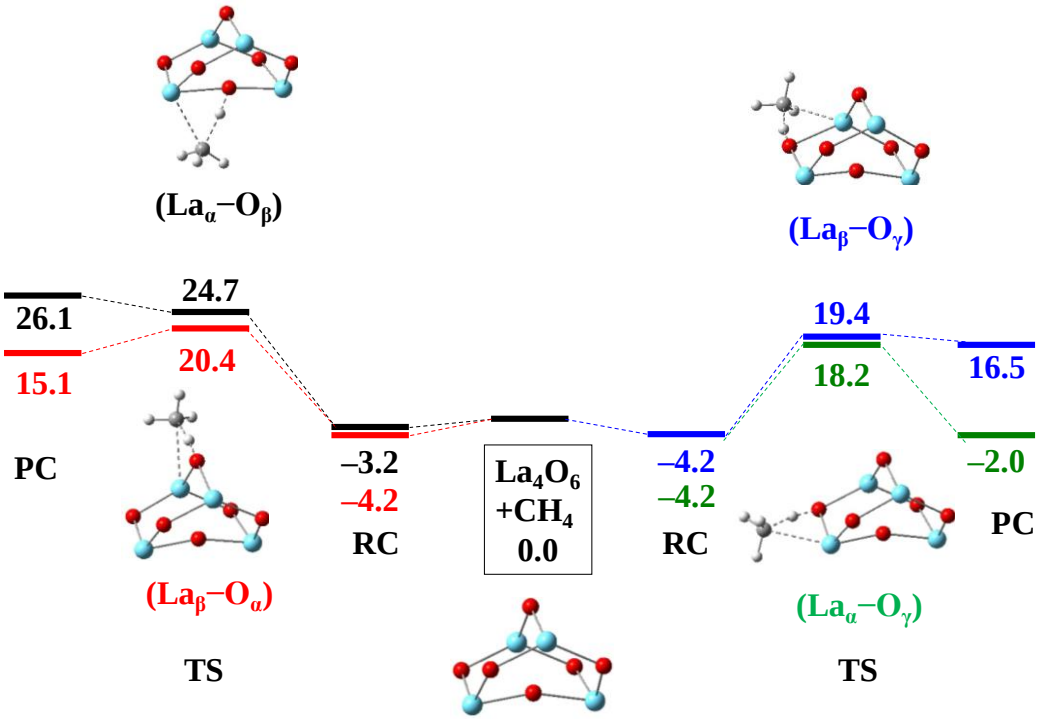
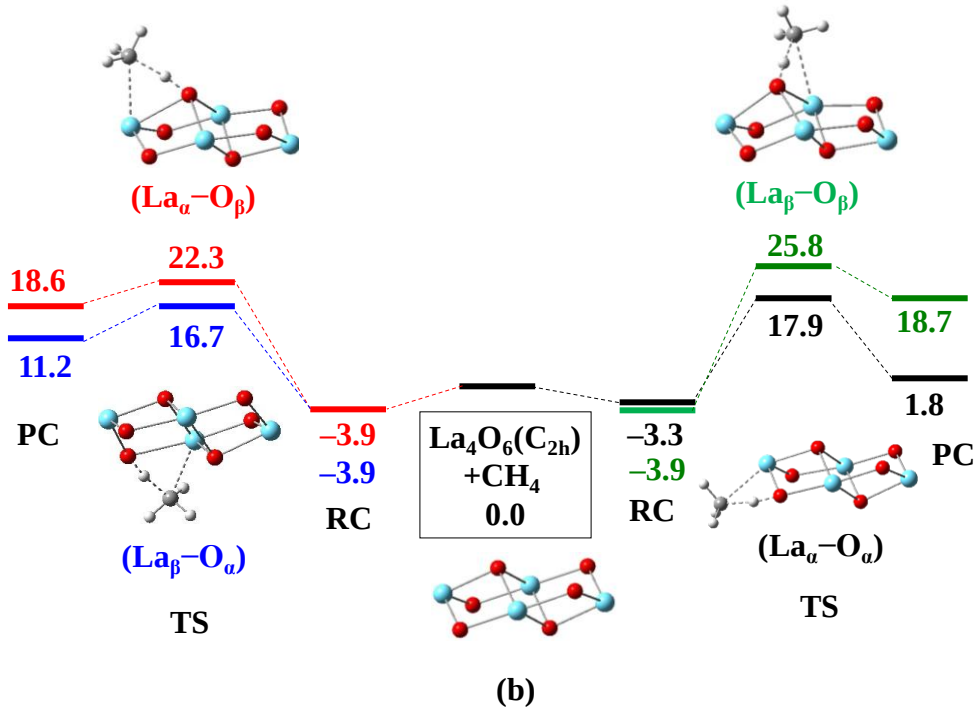


Figure S3. Potential Energy Surfaces for CH_4 Activation by (a) La_4O_6 (C_{2v}) and (b) La_4O_6(C_{2h}) with Relative Energies at 0 K Calculated at the CCSD(T)/aVDZ Level Shown in kcal/mol.





Section 3.

Table S1. Cartesian Coordinates in Angstroms Optimized at the B3LYP/aVDZ Level for Structures Shown by **Figure S1**.

La_2O_3H (C_s)
Charge: +1 Spin Multiplicity: 1

La	0.05815600	0.02447900	1.56440900
O	0.05815600	1.46448800	0.00000000
La	0.05815600	0.02447900	-1.56440900
O	1.05159300	-1.00082300	0.00000000
O	-1.61840400	-0.74565300	0.00000000
H	-2.56051300	-0.53467300	0.00000000

$La_3O_4H(OH)$
(O_α)
Charge: +1 Spin Multiplicity: 1

La	1.59717900	1.46069800	0.16701000
O	2.24543800	-0.35378000	-0.60321400
O	0.12817200	0.10598000	1.04716500
La	0.81239500	-1.90642700	0.05649000
O	-1.00582600	-1.57952500	-0.87043700
La	-1.94481100	0.31518400	-0.17872200
O	-0.36324400	2.11767700	-0.95532800
O	-3.69233600	0.26432100	1.05709700
H	-4.46090800	0.17200000	1.62773100
H	-0.52825700	2.83166800	-1.58233700

(O_β)
Charge: +1 Spin Multiplicity: 1

La	0.39874400	-1.04315900	1.84534700
O	1.83781400	-1.68957500	0.00000000
O	-0.78281500	-0.74004600	0.00000000
La	0.39874400	-1.04315900	-1.84534700
O	0.39874400	0.96886800	-1.88111700
La	-0.66129900	1.80434000	0.00000000
O	0.39874400	0.96886800	1.88111700
O	-2.71402000	2.40949800	0.00000000
H	-3.65295900	2.61646700	0.00000000
H	2.78239800	-1.88466700	0.00000000

(O_γ)
Charge: +1 Spin Multiplicity: 1

La	0.35947600	-1.13821500	1.76084100
O	1.42916700	-1.70584300	0.00000000
O	-1.25861900	-1.14029900	0.00000000
La	0.35947600	-1.13821500	-1.76084100
O	0.35947600	0.95698100	-1.64949000
La	-0.39965700	2.17289200	0.00000000

O	0.35947600	0.95698100	1.64949000
O	-2.48796800	1.52647100	0.00000000
H	-3.44597200	1.61176400	0.00000000
H	-1.96602800	-0.46439300	0.00000000

La_4O_6H
(La_4O_6 (T_d))
Charge: +1 Spin Multiplicity: 1

O	1.61280600	1.62107100	-0.05752800
La	0.00000000	2.08181400	-1.32293500
La	1.95554800	0.00000000	1.39306000
O	-1.61280600	1.62107100	-0.05752800
O	0.00000000	0.00000000	-2.61415100
O	0.00000000	0.00000000	2.29233500
O	1.61280600	-1.62107100	-0.05752800
La	-1.95554800	0.00000000	1.39306000
La	0.00000000	-2.08181400	-1.32293500
O	-1.61280600	-1.62107100	-0.05752800
H	0.00000000	0.00000000	-3.57873400

La_4O_6H
(La_4O_6 (C_{2v}), O_α)
Charge: +1 Spin Multiplicity: 1

La	0.00000000	2.29982800	-1.08846400
O	1.76603000	2.01585500	0.05311100
O	0.00000000	0.00000000	2.39953600
O	0.00000000	0.00000000	-0.67597700
La	1.91001500	0.00000000	0.92310200
O	1.76603000	-2.01585500	0.05311100
La	0.00000000	-2.29982800	-1.08846400
O	-1.76603000	2.01585500	0.05311100
La	-1.91001500	0.00000000	0.92310200
O	-1.76603000	-2.01585500	0.05311100
H	0.00000000	0.00000000	3.36318600

La_4O_6H
(La_4O_6 (C_{2v}), O_β)
Charge: +1 Spin Multiplicity: 1

La	1.04785700	2.50553000	0.00000000
O	-0.05654700	2.14452600	1.74002600
O	-2.04659500	0.01918000	0.00000000
O	0.97403300	0.09189600	0.00000000
La	-0.93769800	0.02403200	1.85412400
O	-0.05654700	-2.01771800	1.78435900
La	0.97662300	-2.59919300	0.00000000
O	-0.05654700	2.14452600	-1.74002600
La	-0.93769800	0.02403200	-1.85412400

O	-0.05654700	-2.01771800	-1.78435900
H	1.89215700	-0.31839400	0.00000000

La_4O_6H
(La_4O_6 (C_{2v}), O_γ)
Charge: +1 Spin Multiplicity: 1

La	2.14617600	-0.34272500	-1.15532200
O	2.14127100	-1.97766900	0.54053000
O	0.11412400	0.28560200	1.97794400
O	0.03096600	-0.84373200	-1.05957100
La	-0.29477700	-1.68463300	1.27968300
O	-2.28653800	-1.32976800	0.44938300
La	-2.14541300	-0.03828200	-1.21251300
O	1.92531200	1.56565100	-0.37258900
La	0.18533600	2.17015600	0.90958900
O	-1.50652900	1.83830800	-0.40504100
H	2.84578200	-2.26458100	1.13282600

La_4O_6H
(La_4O_6 (C_{2h}), O_α)
Charge: +1 Spin Multiplicity: 1

La	-3.05942200	-0.10685200	-0.08068000
O	-1.97618800	-1.78155800	-0.75190200
O	-1.04823000	0.02766000	1.17462700
O	0.96195700	0.13079800	-0.91542800
La	0.02819600	-1.76079500	0.21208500
O	2.36200800	-1.71568400	0.58563000
La	3.08185100	-0.04698400	-0.29495200
O	-2.14148400	1.69941300	-0.77204900
La	-0.16653900	1.83245000	0.11840300
O	2.32095600	1.91465300	0.81917400
H	2.77491800	2.48209800	1.45276600

La_4O_6H
(La_4O_6 (C_{2h}), O_β)
Charge: +1 Spin Multiplicity: 1

La	1.46433400	2.56306400	0.00000000
O	0.37961800	2.01173100	1.73318100
O	1.63853500	0.18158600	0.00000000
O	-1.37056700	0.11923100	0.00000000
La	0.37961800	-0.19246400	1.87975600
O	-0.84086800	-2.06187700	1.65361700
La	-2.10229500	-2.22442400	0.00000000
O	0.37961800	2.01173100	-1.73318100
La	0.37961800	-0.19246400	-1.87975600
O	-0.84086800	-2.06187700	-1.65361700
H	-1.67641600	1.03421700	0.00000000

La_6O_9H

Charge: +1 Spin Multiplicity: 1

La	-1.90871200	-1.58752900	0.00000000
La	-1.15792300	1.26384900	1.80555400
O	-2.53272900	0.66974500	0.00000000
La	-1.15792300	1.26384900	-1.80555400
La	1.13915200	-1.32057900	1.76460000
O	0.21840900	-2.50878300	0.00000000
La	1.13915200	-1.32057900	-1.76460000
O	-1.15792300	-0.96895700	2.14827800
O	1.14909500	0.99492500	2.13669000
O	-0.01796400	0.19833900	0.00000000
La	1.96062000	1.53726500	0.00000000
O	2.54392900	-0.64276900	0.00000000
O	-1.15792300	-0.96895700	-2.14827800
O	-0.25435700	2.91373200	0.00000000
O	1.14909500	0.99492500	-2.13669000
H	-0.33589100	3.87468600	0.00000000

La_2O_3F

Charge: -1 Spin Multiplicity: 1

La	-0.29486800	1.26772300	0.00000000
O	-0.72146500	-0.49365700	1.40199400
La	0.38204000	-1.69751900	0.00000000
O	-0.72146500	-0.49365700	-1.40199400
O	1.63347800	0.05846700	0.00000000
F	-0.72146500	3.54768500	0.00000000

$La_3O_4(OH)F$

Charge: -1 Spin Multiplicity: 1

La	0.09010300	2.15369300	0.15029900
O	1.79501700	1.27062400	-0.78067900
O	0.01250300	0.16037100	1.16633900
La	1.73972700	-0.90907600	-0.09911600
O	-0.06670200	-1.86199200	-0.92795200
La	-1.80205200	-0.77805800	-0.11084000
O	-1.67209800	1.42014800	-0.78104900
O	-3.70657100	-1.76638400	0.73901800
H	-4.34930400	-2.36763600	1.12251300
F	3.54097300	-2.00093200	0.77249800

La_4O_6F

($La_4O_6(T_d)$)

Charge: -1 Spin Multiplicity: 1

O	0.00000000	1.99151100	1.16180000
La	0.00000000	0.00000000	2.28813200
La	0.00000000	2.24039600	-0.94679600
O	1.72469900	-0.99575500	1.16180000
O	-1.72469900	-0.99575500	1.16180000

O	1.69331600	0.97763600	-1.56183200
O	-1.69331600	0.97763600	-1.56183200
La	1.94024000	-1.12019800	-0.94679600
La	-1.94024000	-1.12019800	-0.94679600
O	0.00000000	-1.95527300	-1.56183200
F	0.00000000	0.00000000	4.56437900

La_4O_6F
($La_4O_6(C_{2v})$, La_α)
Charge: -1 Spin Multiplicity: 1

La	-1.80718700	-1.63189700	0.00000000
O	-0.61991300	-1.81231400	1.88459000
O	2.17290300	-0.88950300	0.00000000
O	-0.51954800	0.36931000	0.00000000
La	1.03715600	-0.35226300	1.79764500
O	1.03715600	1.99679400	1.77149400
La	0.02576300	2.56444200	0.00000000
O	-0.61991300	-1.81231400	-1.88459000
La	1.03715600	-0.35226300	-1.79764500
O	1.03715600	1.99679400	-1.77149400
F	-4.06637000	-1.30969600	0.00000000

La_4O_6F
($La_4O_6(C_{2v})$, La_β)
Charge: -1 Spin Multiplicity: 1

La	1.22698400	-0.09449700	2.21313900
O	0.05765400	-1.87703500	2.17959500
O	-1.98128900	-0.30313400	0.00000000
O	1.33824100	-0.50636600	0.00000000
La	-0.72307400	-2.00346000	0.00000000
O	0.05765400	-1.87703500	-2.17959500
La	1.22698400	-0.09449700	-2.21313900
O	0.05765400	1.63553300	1.92065300
La	-1.23623200	1.82238500	0.00000000
O	0.05765400	1.63553300	-1.92065300
F	-2.76625400	3.49266400	0.00000000

La_4O_6F
($La_4O_6(C_{2h})$, La_α)
Charge: -1 Spin Multiplicity: 1

La	-1.48777900	-2.83044800	0.00000000
O	-0.36526100	-2.52694200	1.76960700
O	-1.43314400	-0.56545800	0.00000000
O	1.39134500	0.29165300	0.00000000
La	0.04325100	-0.17732500	1.78011100
O	0.04325100	2.02989000	1.88018500
La	1.06319000	2.69528100	0.00000000
O	-0.36526100	-2.52694200	-1.76960700
La	0.04325100	-0.17732500	-1.78011100

O	0.04325100	2.02989000	-1.88018500
F	2.75083300	4.22920000	0.00000000

La_4O_6F
($La_4O_6(C_{2h})$, La_β)
Charge: -1 Spin Multiplicity: 1

La	2.95295900	-0.28763500	0.11087200
O	2.03158500	-2.17661700	0.56230400
O	1.04871200	-0.05969300	-1.14967300
O	-0.96674700	-0.32939400	1.10420800
La	-0.10852100	-1.86694500	-0.28106100
O	-2.34567900	-1.75335600	-0.89174300
La	-3.01089700	-0.06843100	0.27833700
O	2.09043100	1.28068200	1.16628000
La	0.09954900	1.81079500	-0.01297100
O	-2.22571700	1.76463500	-0.38100800
F	0.75035600	3.74292000	-0.96756700

La_6O_9F
Charge: -1 Spin Multiplicity: 1

La	0.00000000	2.43508100	0.11108900
La	2.43508100	0.00000000	0.11108900
O	1.54735900	1.54735900	-1.37085000
La	0.00000000	0.00000000	-2.48683100
La	0.00000000	0.00000000	2.58395400
O	-1.54551000	1.54551000	1.69248000
La	-2.43508100	0.00000000	0.11108900
O	1.54551000	1.54551000	1.69248000
O	1.54551000	-1.54551000	1.69248000
O	0.00000000	0.00000000	0.19599800
La	0.00000000	-2.43508100	0.11108900
O	-1.54551000	-1.54551000	1.69248000
O	-1.54735900	1.54735900	-1.37085000
O	1.54735900	-1.54735900	-1.37085000
O	-1.54735900	-1.54735900	-1.37085000
F	0.00000000	0.00000000	-4.74715600

Table S2. Cartesian Coordinates in Angstroms Optimized at the B3LYP/aVDZ Level for the Structures Shown in **Figure S2**.

La_2O_3, D_{3h}

LA	0.000000	0.000000	1.502187
O	0.000000	1.567729	0.000000
LA	0.000000	0.000000	-1.502187
O	1.357693	-0.783865	0.000000
O	-1.357693	-0.783865	0.000000

$La_3O_4(OH)$, C_s

LA	0.447866	-1.086245	1.729211
O	1.617031	-1.693433	0.000000
O	-0.974361	-0.661739	0.000000
LA	0.447866	-1.086245	-1.729211
O	0.447866	0.993385	-1.826239
LA	-0.692825	1.748039	0.000000
O	0.447866	0.993385	1.826239
O	-2.559540	2.963467	0.000000
H	-3.396669	3.433179	0.000000

La_4O_6, T_d

O	0.000000	0.000000	2.352531
LA	1.375511	1.375511	1.375511
LA	-1.375511	-1.375511	1.375511
O	0.000000	2.352531	0.000000
O	2.352531	0.000000	0.000000
O	-2.352531	0.000000	0.000000
O	0.000000	-2.352531	0.000000
LA	-1.375511	1.375511	-1.375511
LA	1.375511	-1.375511	-1.375511
O	0.000000	0.000000	-2.352531

La_4O_6, C_{2v}

LA	0.000000	2.283099	-1.102119
O	1.757461	2.077276	0.052128
O	0.000000	0.000000	2.175824
O	0.000000	0.000000	-0.828807
LA	1.809124	0.000000	0.992959

O	1.757461	-2.077276	0.052128
LA	0.000000	-2.283099	-1.102119
O	-1.757461	2.077276	0.052128
LA	-1.809124	0.000000	0.992959
O	-1.757461	-2.077276	0.052128

La_4O_6, C_{2h}

LA	1.045471	2.846376	0.000000
O	0.000000	2.296147	1.754032
O	1.363859	0.554043	0.000000
O	-1.363859	-0.554043	0.000000
LA	0.000000	0.000000	1.783019
O	0.000000	-2.296147	1.754032
LA	-1.045471	-2.846376	0.000000
O	0.000000	2.296147	-1.754032
LA	0.000000	0.000000	-1.783019
O	0.000000	-2.296147	-1.754032

La_6O_9, O_h

LA	0.000000	0.000000	2.458448
LA	0.000000	2.458448	0.000000
O	-1.527851	1.527851	1.527851
LA	-2.458448	0.000000	0.000000
LA	2.458448	0.000000	0.000000
O	1.527851	-1.527851	1.527851
LA	0.000000	-2.458448	0.000000
O	1.527851	1.527851	1.527851
O	1.527851	1.527851	-1.527851
O	0.000000	0.000000	0.000000
LA	0.000000	0.000000	-2.458448
O	1.527851	-1.527851	-1.527851
O	-1.527851	-1.527851	1.527851
O	-1.527851	1.527851	-1.527851
O	-1.527851	-1.527851	-1.527851

$La_2O_2(CO_3)$

La	0.88252700	-1.44614700	0.00000000
La	0.06310000	1.69338000	0.00000000
O	0.88252700	0.23056200	1.34331500
O	0.88252700	0.23056200	-1.34331500

O	-1.90571500	0.66712300	0.00000000
O	-1.33698300	-1.51597600	0.00000000
O	-3.51084800	-0.91659500	0.00000000
C	-2.33213400	-0.60961800	0.00000000

$La_3O_3(CO_3)(OH)$ (**La_α–O_α**)

La	-1.64612500	1.02013100	-0.57338900
O	0.46567200	0.28141500	-1.14450200
La	0.80633800	-1.78575500	-0.00364300
O	1.99787500	-0.28940100	1.13717800
La	1.67867400	1.59686500	0.27051200
O	-0.35853200	2.28558300	0.58807300
C	-2.79182400	-1.21800600	0.83985400
O	-3.26386600	-2.17433300	1.42318000
O	-1.49405100	-1.22354300	0.36140800
O	-3.37418800	-0.06834100	0.55922900
O	1.85587600	-3.32074400	-1.16131900
H	2.30410700	-3.99777300	-1.67342300

$La_3O_3(CO_3)(OH)$ (**La_α–O_β**)

La	-1.07229100	-1.59013300	-0.46022900
O	0.34599000	0.12565800	-1.18472800
La	2.12451400	-0.31977400	0.43561600
O	1.22910600	1.77005600	0.91081200
La	-0.36214300	2.03321800	-0.33404500
O	-2.06477700	0.58857300	0.25489200
C	-3.21735100	-0.00555700	0.76441400
O	-3.16209700	-1.30518600	0.62073700
O	0.56255100	-1.92403600	0.76822200
O	-4.10701100	0.67253600	1.24311900
O	4.08075700	-0.69250300	-0.50782000
H	4.89338800	-0.87614700	-0.98483400

$La_4O_5(CO_3)$ ($La_4O_6(T_d)$)

O	-2.105605	0.700186	-0.000162
LA	-1.517077	-1.791051	0.000146
O	-4.287880	1.324708	-0.001230
LA	-0.455240	2.337237	-0.004236
O	0.710754	1.644786	1.628666
O	-0.139593	-1.564509	-1.674477

O	0.715704	1.639798	-1.631556
LA	1.620156	-0.348886	-1.947203
O	-0.141388	-1.563767	1.675828
O	2.547861	-0.598736	0.003940
C	-3.461166	0.422003	-0.001445
LA	1.614489	-0.342891	1.951652
O	-3.698063	-0.861629	-0.002490

$La_4O_5(CO_3)$ ($La_4O_6(C_{2v})$, **La_α–O_γ**)

La	-2.43579600	-0.43166100	-1.22317500
O	-2.74702400	1.16110000	0.12473300
O	-0.29383800	-0.26790100	2.16844500
O	-0.23022000	0.06559100	-0.77264300
La	-0.84870600	1.62967400	1.24935400
O	1.06326100	2.39796100	0.31303300
La	1.89107000	1.03659100	-1.03655200
O	-1.85212200	-2.19216100	-0.18796000
La	0.11256500	-1.85351200	0.80215500
O	2.22936300	-1.22052900	-0.15748000
C	3.59245500	-1.07400400	-0.01600500
O	3.97441000	0.11797600	-0.42394000
O	4.28800900	-1.97181100	0.43137300

$La_4O_5(CO_3)$ ($La_4O_6(C_{2v})$, **La_β–O_γ**)

LA	-2.270865	-0.983412	-1.149365
O	-2.905715	0.470842	0.276008
O	-0.058921	-0.130936	2.112179
O	-0.258134	0.175213	-0.901610
LA	-1.196984	1.476103	1.300700
O	0.454323	2.730308	0.246397
LA	1.442259	1.585975	-1.135409
O	-1.155409	-2.485629	-0.221881
LA	0.731527	-1.635542	0.736141
O	2.578498	-0.173403	-0.258040
C	3.595165	-1.074754	0.077593
O	4.755463	-0.798169	-0.188161
O	3.113715	-2.139415	0.643433

$La_4O_5(CO_3)$ ($La_4O_6(C_{2v})$, **La_β–O_α**)

La	1.19611700	0.64810000	2.26590200
O	1.19611700	-1.47993100	2.02473000
O	-1.65352600	-1.17072200	0.00000000
O	0.93981600	0.44692900	0.00000000
La	0.48302800	-2.03271900	0.00000000
O	1.19611700	-1.47993100	-2.02473000
La	1.19611700	0.64810000	-2.26590200
O	-0.67693500	1.58733600	2.05254700
La	-1.59377100	1.27680300	0.00000000
O	-0.67693500	1.58733600	-2.05254700
C	-3.04586900	-1.25054200	0.00000000
O	-3.59466400	-2.34114000	0.00000000
O	-3.57620800	-0.06150300	0.00000000

$La_4O_5(CO_3)$ ($La_4O_6(C_{2h})$, **La_α–O_α**)

La	2.75639100	0.76159300	-0.46338700
O	2.23271800	-1.55326100	0.23468400
O	0.54782200	0.32644700	-1.11468200
O	-1.21015800	-0.22551800	1.13272700
La	-0.13281900	-1.67186600	-0.28502200
O	-2.25095300	-1.82052900	-0.93556300
La	-3.32160800	-0.32396600	0.14917100
O	1.70352900	2.21139500	0.60894000
La	-0.54094600	1.82458100	0.27545600
O	-2.71525700	1.60355800	-0.41514800
C	3.45253600	-1.73766800	0.85284800
O	3.73514200	-2.78977200	1.40226000
O	4.19550700	-0.65525300	0.75409900

$La_4O_5(CO_3)$ ($La_4O_6(C_{2h})$, **La_β–O_α**)

La	-2.78796000	-0.96831000	-0.29384100
O	-1.54628000	3.16487300	0.57464100
O	-0.77061700	-0.56378900	-1.14665600
O	1.06725000	0.13797200	1.05380800
La	-0.04669500	1.59753200	-0.40322900
O	2.12188400	1.80369100	-0.95881500
La	3.19343800	0.36641300	0.16296000
O	-1.72532100	-2.35967200	0.76758600
La	0.54291900	-1.91731300	0.23727700
O	2.68026800	-1.61273900	-0.41963400

C	-2.65913900	2.50740800	0.78888900
O	-3.70359700	2.93529300	1.25230000
O	-2.55386200	1.18077700	0.40003900

$La_4O_5(CO_3)$ ($La_4O_6(C_{2h})$, **La_α–O_β**)

La	0.32427700	-2.90699600	0.00000000
O	0.80382200	-1.81128200	1.78048900
O	-1.37421700	-0.77709100	0.00000000
O	1.06039500	0.79768900	0.00000000
La	-0.12200800	0.21165600	1.87679600
O	-0.12200800	2.47130100	1.81890300
La	0.82885400	3.05118600	0.00000000
O	0.80382200	-1.81128200	-1.78048900
La	-0.12200800	0.21165600	-1.87679600
O	-0.12200800	2.47130100	-1.81890300
C	-2.46404100	-1.66904700	0.00000000
O	-3.60112400	-1.22410600	0.00000000
O	-2.07809700	-2.90819800	0.00000000

$La_6O_8(CO_3)$ ($La_6O_9(O_h)$)

LA	1.194379	-1.026710	1.796399
LA	-1.139534	1.517559	1.737169
O	-1.091655	-0.771417	2.156055
LA	-1.904953	-1.420890	0.000000
LA	1.892559	1.835040	0.000000
O	2.579577	-0.403425	0.000000
LA	1.194379	-1.026710	-1.796399
O	1.194379	1.216984	2.168673
O	-0.216650	2.791967	0.000000
O	0.049089	0.112951	0.000000
LA	-1.139534	1.517559	-1.737169
O	1.194379	1.216984	-2.168673
O	0.355994	-2.602505	0.000000
O	-2.547364	0.900974	0.000000
O	-1.091655	-0.771417	-2.156055
C	-0.207012	-3.892388	0.000000
O	-1.500617	-3.851190	0.000000
O	0.536555	-4.866020	0.000000

Table S3. Cartesian Coordinates in Angstroms Optimized at the B3LYP/aVDZ Level for Structures on Potential Energy Surfaces Shown by **Figure S3**.

La_4O_6 (C_{2v})

(La_α–O_β)

RC

La	2.09387900	1.31778100	0.43275900
O	2.10949600	0.77373400	-1.60460300
O	0.50960200	-2.15732900	-0.72739200
O	-0.09232300	0.63037200	0.21384800
La	0.26205400	-0.48299200	-2.07149900
O	-1.95899900	-0.03076300	-1.85405800
La	-2.38637400	0.43306300	0.16783800
O	2.13039300	-0.35143600	1.72754500
La	0.28432200	-1.63600300	1.36210000
O	-1.93711400	-1.15223900	1.49731000
C	-2.05737300	3.92519600	1.21765400
H	-2.84354200	4.00339300	0.45552100
H	-1.26157900	3.24845000	0.87614600
H	-1.62851000	4.92091700	1.38083000
H	-2.48181100	3.56193600	2.16207300

TS

La	2.40033500	-0.07399800	1.12669400
O	2.18402800	1.72531300	0.06681500
O	0.20029400	0.13102700	-2.18566900
O	0.03185500	-0.04544200	0.82101200
La	0.14191900	1.90177400	-0.95622900
O	-1.97047800	1.81417200	-0.19885100
La	-2.52931400	-0.02219400	0.72188500
O	2.16081500	-1.74251200	-0.11671500
La	0.11982900	-1.76803200	-1.16199100
O	-2.00234400	-1.72921300	-0.42755300
C	-1.29778200	-0.33509500	3.17653000
H	-1.91079900	0.48039900	3.61443700
H	-0.44154000	-0.15872700	1.82404400
H	-0.41454200	-0.39683900	3.83898500
H	-1.84758200	-1.28138300	3.36058800

PC

La	-0.11605300	2.71669200	0.00000000
O	-0.99738200	1.95953200	1.74002600
O	-2.01952700	-0.76674800	0.00000000
O	0.74195600	0.45950300	0.00000000
La	-0.99738200	-0.33675200	1.85412400

O	0.59979100	-1.88407400	1.78435900
La	1.77699700	-2.02457800	0.00000000
O	-0.99738200	1.95953200	-1.74002600
La	-0.99738200	-0.33675200	-1.85412400
O	0.59979100	-1.88407400	-1.78435900
C	3.62228000	-0.07758000	0.00000000
H	4.20607100	-0.40163800	0.88768600
H	1.74723400	0.43293300	0.00000000
H	3.71678300	1.02567100	0.00000000
H	4.20607100	-0.40163800	-0.88768600

(La_{α}–O_{β})

RC

La	1.10413600	0.54449400	2.27625400
O	1.10413600	-1.56163500	2.07106800
O	-1.65015100	-1.23416400	0.00000000
O	0.88422200	0.39476600	0.00000000
La	0.33060200	-2.11135500	0.00000000
O	1.10413600	-1.56163500	-2.07106800
La	1.10413600	0.54449400	-2.27625400
O	-0.82559200	1.39106200	2.07757200
La	-1.65186500	0.92910900	0.00000000
O	-0.82559200	1.39106200	-2.07757200
C	-4.88305500	1.47521000	0.00000000
H	-4.47769500	1.95076000	0.90412900
H	-4.47769500	1.95076000	-0.90412900
H	-4.66467400	0.39832600	0.00000000
H	-5.97045000	1.60892700	0.00000000

TS

La	1.07505600	0.59271600	2.27158400
O	1.07505600	-1.52004500	2.06560000
O	-1.72756100	-1.30409200	0.00000000
O	0.85343100	0.39104800	0.00000000
La	0.35222300	-2.06964300	0.00000000
O	1.07505600	-1.52004500	-2.06560000
La	1.07505600	0.59271600	-2.27158400
O	-0.83367100	1.47675800	2.04216100
La	-1.71767100	1.06427900	0.00000000
O	-0.83367100	1.47675800	-2.04216100
C	-4.16566900	-0.16886400	0.00000000
H	-4.49983800	0.40248000	0.89159200
H	-4.49983800	0.40248000	-0.89159200
H	-2.82255400	-0.97345300	0.00000000
H	-4.77875800	-1.08528600	0.00000000

PC

La	-0.69649800	-2.21883800	-1.04553800
O	-1.73459900	-2.05548000	0.82348700
O	0.61463000	0.12015300	2.22025100
O	-1.08872100	0.01577900	-0.91866600
La	-1.66105500	0.07523500	1.43588200
O	-1.60484500	2.19404300	0.75163700
La	-0.53370500	2.21727100	-1.10545200
O	1.34795800	-1.92229200	-0.61965200
La	2.23364300	-0.09042200	0.32520200
O	1.48370000	1.75862700	-0.70532900
C	4.79891000	-0.08463600	0.75063400
H	5.29875200	-1.03634400	0.47993400
H	5.30939000	0.70243200	0.15857500
H	0.85422700	0.79950500	2.86309400
H	5.08323700	0.11053500	1.80537100

(La_{β}–O_{γ})

PC

La	2.22538000	0.95789300	-0.99814000
O	2.77703400	-0.25927000	0.63634100
O	-0.30839100	0.38412700	2.02195200
O	0.31547000	-0.31163600	-0.83167500
La	0.92257100	-1.30175500	1.46077300
O	-0.57298600	-2.70407600	0.46983900
La	-1.48226800	-1.69826100	-1.16022000
O	0.84881000	2.48558200	-0.48302500
La	-1.05197500	1.53090800	0.34246500
O	-2.52330400	0.05677600	-0.60533400
C	-3.92285200	3.18997400	1.05632800
H	-3.51775700	2.96075600	2.05131800
H	-3.29589900	3.93949700	0.55395400
H	-3.99709200	2.27477200	0.45319300
H	-4.92658400	3.61239700	1.18069200

TS

La	2.31332800	0.56673500	-1.06849000
O	2.63835500	-0.91099600	0.41592000
O	-0.13884900	0.26348700	2.08909900
O	0.14563200	-0.23320600	-0.88000100
La	0.68709300	-1.56782700	1.34395000
O	-1.13732400	-2.51214900	0.30830300
La	-1.85407000	-1.23688300	-1.17068900
O	1.39688700	2.29058900	-0.27850300
La	-0.63528100	1.76813900	0.59772500
O	-2.63196200	0.66597100	-0.43291900
C	-3.08806900	3.06034800	0.74003500
H	-3.00662000	3.12222800	1.84713600
H	-2.65173300	4.00318400	0.34391800

H	-2.95770000	1.64337500	0.01947300
H	-4.16844300	3.14015500	0.53177700

PC

La	-0.29775400	2.27381700	-1.09954900
O	0.65975400	2.55781000	0.78803300
O	-0.60538300	-0.38783800	1.79377200
O	0.88290400	0.30075900	-1.04187100
La	1.25901400	0.60386200	1.67855400
O	2.48023500	-1.20386900	0.81632400
La	1.69355700	-1.67833400	-1.00872300
O	-2.06388600	1.16430300	-0.83261600
La	-2.04829200	-0.83472300	0.19148000
O	-0.52457600	-2.58543500	-0.89187400
C	-4.35614600	-1.73431900	1.00152700
H	-4.33520300	-2.09979300	2.04798900
H	-5.15264000	-0.96363400	0.97000900
H	-0.83602400	-3.49745900	-0.90017300
H	-4.74353400	-2.58246200	0.39845300

(La_{α}–O_{γ})

RC

La	2.46459200	0.00193500	-1.12535000
O	2.27679200	-1.75717500	0.03036200
O	0.21786400	-0.00096200	2.17983600
O	0.18677600	0.00093000	-0.82093300
La	0.20887200	-1.80848200	0.99322400
O	-1.88098600	-1.76316700	0.08011500
La	-2.10942600	-0.00124000	-1.06844400
O	2.27482300	1.75955900	0.03210100
La	0.20638400	1.80735000	0.99412000
O	-1.88407500	1.75990300	0.08177300
C	-5.33977000	0.00324200	-0.09219200
H	-4.78150900	-0.90009400	0.19058000
H	-6.29663700	0.00406000	0.44288900
H	-4.77821700	0.90374900	0.19303000
H	-5.54864300	0.00509900	-1.17171600

TS

La	2.35797000	-0.21184400	1.21926300
O	2.40742700	1.54194000	0.04378500
O	0.26474100	-0.03025700	-2.19221500
O	0.10151300	0.00314900	0.77590600
La	0.42872300	1.79529800	-1.03757300
O	-1.66765600	2.05066200	-0.15872300
La	-2.18372500	0.38274400	0.98391100

O	2.05531900	-1.94399500	0.04762000
La	0.05235000	-1.80937500	-0.99311600
O	-2.09122900	-1.63045500	-0.15290200
C	-4.59799700	-0.84349300	0.35102600
H	-4.96831000	0.07739400	-0.14448400
H	-5.17026700	-1.66877600	-0.10365300
H	-3.24028700	-1.41801000	-0.00342600
H	-4.94716000	-0.79688400	1.40595600

PC

La	-1.84558400	-0.83962800	1.41651000
O	-1.77238700	-2.00106500	-0.32911600
O	-0.69901100	0.88663500	-2.10615800
O	0.11792900	-0.02846700	0.51426700
La	-0.15860900	-1.22548100	-1.73476900
O	2.01422700	-1.22931400	-1.22934100
La	2.40901800	0.00301300	0.45812800
O	-2.37093600	1.17138100	0.91741800
La	-0.74483900	2.04511900	-0.32069200
O	1.66783000	2.38980600	0.26519100
C	2.81601900	-1.23306400	2.73229100
H	3.78508100	-1.76999000	2.78388800
H	2.80182000	-0.56346500	3.61576800
H	2.18655000	3.19861400	0.32167700
H	2.05001800	-2.01087700	2.93382600

La_4O_6 (C_{2h})

(La_α–O_β)

RC

La	1.22708500	2.92561700	0.00000000
O	0.18090000	2.37769900	1.75352100
O	1.54939100	0.62943300	0.00000000
O	-1.19588000	-0.43433700	0.00000000
La	0.18090000	0.07965900	1.78244100
O	0.09813200	-2.21283900	1.76573100
La	-0.94853500	-2.74083700	0.00000000
O	0.18090000	2.37769900	-1.75352100
La	0.18090000	0.07965900	-1.78244100
O	0.09813200	-2.21283900	-1.76573100
C	-4.37384300	-2.38187100	0.00000000
H	-3.72028500	-1.49779400	0.00000000
H	-5.41740000	-2.04641100	0.00000000
H	-4.20591600	-2.98834400	-0.90093400
H	-4.20591600	-2.98834400	0.90093400

TS

La	-0.45167500	-2.96396300	0.00000000

O	0.34890300	-2.08457200	1.76791200
O	-1.39901000	-0.53111300	0.00000000
O	1.27222600	0.70555000	0.00000000
La	-0.02749800	0.14560900	1.81829000
O	-0.02749800	2.43283200	1.77040700
La	0.99450700	2.99026900	0.00000000
O	0.34890300	-2.08457200	-1.76791200
La	-0.02749800	0.14560900	-1.81829000
O	-0.02749800	2.43283200	-1.77040700
C	-3.17616200	-2.56402500	0.00000000
H	-4.07684900	-1.92748900	0.00000000
H	-3.29071400	-3.21782000	0.89046600
H	-3.29071400	-3.21782000	-0.89046600
H	-2.21966400	-1.31925000	0.00000000

PC

La	-1.86277000	-2.28939400	0.00000000
O	-0.59626000	-1.97358600	1.78571500
O	-1.15735000	0.12421800	0.00000000
O	1.81084000	0.31975800	0.00000000
La	0.49538900	-0.10653600	1.88126700
O	0.49538900	2.16016200	1.75540500
La	1.56176500	2.65710100	0.00000000
O	-0.59626000	-1.97358600	-1.78571500
La	0.49538900	-0.10653600	-1.88126700
O	0.49538900	2.16016200	-1.75540500
C	-4.44500700	-1.83539700	0.00000000
H	-4.80031500	-1.26715400	0.88319500
H	-5.03995100	-2.77418600	0.00000000
H	-4.80031500	-1.26715400	-0.88319500
H	-1.62039300	0.96962000	0.00000000

(La_{β}–O_{α})

RC

La	-3.02380700	-0.20845300	0.19041500
O	-2.17774200	-1.77047100	-0.95785900
O	-0.93011400	-0.37047000	1.14579800
O	0.97693600	0.05777700	-1.06114500
La	0.01929200	-1.90380000	-0.29433500
O	2.18732500	-2.00503300	0.45999800
La	3.03553000	-0.12211100	-0.00962000
O	-2.21440800	1.68355700	-0.31333600
La	-0.00579300	1.60246000	0.35292700
O	2.15757400	1.44418500	1.10463000
C	-0.14403400	4.36640400	-1.66383300
H	0.28619200	4.76947500	-0.73582000
H	-1.06398800	3.80005300	-1.45852200
H	-0.38524200	5.20765200	-2.32417200
H	0.59299500	3.72653800	-2.16826100

TS

La	3.01481100	-0.32005300	-0.24059000
O	2.14480300	-1.89063400	0.83339700
O	0.92218600	-0.28106600	-1.10219000
O	-1.01927900	0.05277300	1.09051200
La	-0.09481900	-1.87387100	0.23568100
O	-2.24618700	-1.89628400	-0.54106800
La	-3.07657400	-0.03610600	0.02756000
O	2.43274400	1.64295000	0.46472200
La	-0.03907900	1.68753200	-0.22304000
O	-2.14972200	1.57545400	-0.99579200
C	0.99690300	3.73470000	1.32704300
H	0.61297500	4.49778700	0.61575300
H	1.90025000	2.58228500	0.89007800
H	1.79591500	4.24403600	1.89042900
H	0.18580800	3.56458300	2.06703400

PC

La	-3.08438900	-0.18251300	0.27512200
O	-2.40296200	-1.77037300	-0.83118200
O	-1.05554000	-0.21509300	1.03343800
O	1.03540300	-0.02188200	-1.09319900
La	-0.08042700	-1.84547000	-0.30514600
O	1.97958400	-2.10600800	0.55918100
La	3.03219400	-0.32058000	0.04880900
O	-2.36778800	1.86070900	-0.50585400
La	0.22435800	1.77849100	0.17198400
O	2.24105700	1.33889300	1.07430800
C	0.20185600	4.01080200	-1.21402700
H	-0.54406700	4.74836800	-0.84850900
H	-2.44866500	2.59229400	-1.12696300
H	-0.05306100	3.84362800	-2.28164000
H	1.16763500	4.55507600	-1.22610200

(La_{β}–O_{β})

RC

La	-3.02380700	-0.20845300	0.19041500
O	-2.17774200	-1.77047100	-0.95785900
O	-0.93011400	-0.37047000	1.14579800
O	0.97693600	0.05777700	-1.06114500
La	0.01929200	-1.90380000	-0.29433500
O	2.18732500	-2.00503300	0.45999800
La	3.03553000	-0.12211100	-0.00962000
O	-2.21440800	1.68355700	-0.31333600
La	-0.00579300	1.60246000	0.35292700
O	2.15757400	1.44418500	1.10463000
C	-0.14403400	4.36640400	-1.66383300
H	0.28619200	4.76947500	-0.73582000
H	-1.06398800	3.80005300	-1.45852200
H	-0.38524200	5.20765200	-2.32417200

H	0.59299500	3.72653800	-2.16826100

TS

La	3.00350400	-0.08219500	-0.37111200
O	2.30252900	-1.70690500	0.83402800
O	0.82208800	-0.22986500	-0.95806900
O	-1.17583700	-0.03694600	1.28764100
La	0.07833900	-1.86404200	0.41624500
O	-1.94728500	-1.98613200	-0.65569300
La	-2.98682200	-0.19222900	-0.32618900
O	2.28482700	1.83024600	0.18173600
La	0.02332400	1.81801400	-0.08662600
O	-1.98856200	1.46562400	-1.12709900
C	-0.88575700	2.40525600	2.41960200
H	-1.49984900	3.24042100	2.01786500
H	-1.07935100	0.91893900	1.86145400
H	0.10712300	2.83171400	2.66791900
H	-1.34116600	2.15496300	3.39269600

PC

La	2.72663600	-0.71552100	0.41809200
O	1.38852100	-2.37736300	0.58352600
O	1.04491500	-0.14043600	-1.05700000
O	-1.49439800	-1.37684800	1.35219300
La	-0.35004200	-1.90627800	-0.74505800
O	-2.31497500	-0.85719700	-1.21857200
La	-2.98631200	0.24129600	0.43380300
O	2.08107900	1.09351800	1.27480400
La	0.53195500	2.00258400	-0.09581000
O	-1.67714500	1.85857400	0.46750800
C	1.40602000	4.03921300	-1.47689000
H	-0.91594500	-1.43759300	2.12073500
H	2.21692000	3.76529200	-2.18306700
H	0.63416000	4.54344000	-2.09233600
H	1.83726500	4.83294200	-0.83220800

(La_{α}–O_{α})

RC

La	-2.81940200	0.47853900	-0.09803100
O	-2.17515100	-1.33275000	-0.99731500
O	-0.82051300	0.12033400	1.01385600
O	1.20627900	0.01738800	-1.11510900
La	-0.04814700	-1.68790400	-0.19489800
O	2.06487400	-2.01913000	0.64809700
La	3.19172800	-0.33978000	0.02920300
O	-1.69792800	2.16467900	-0.72442900
La	0.42323200	1.83207300	0.08607600
O	2.53759500	1.46732600	0.91749200
C	-5.14938600	-1.94401200	1.21676900
H	-5.84840100	-1.15511600	0.90584800

H	-4.65330800	-1.65343900	2.15268300
H	-5.72210600	-2.86207400	1.39403300
H	-4.40355900	-2.13492900	0.43222100

TS

La	2.88646900	0.31389800	-0.33525200
O	2.15880300	-1.71001000	0.53558700
O	0.70649600	0.11633000	-1.11307700
O	-1.12722800	-0.08304100	1.15980400
La	-0.08827400	-1.75471400	-0.05277000
O	-2.23473300	-1.81764900	-0.77848700
La	-3.20404000	-0.15274000	0.11364600
O	1.97324000	1.95023000	0.59333700
La	-0.28582800	1.80090700	0.11660000
O	-2.45835400	1.69194900	-0.59557800
C	4.74735300	-1.25739500	1.04074800
H	5.04463100	-0.38124200	1.65406300
H	5.45578700	-1.29933300	0.18551100
H	4.99062600	-2.13611900	1.66093500
H	3.30442400	-1.64035300	0.83551600

PC

La	2.96781000	0.00045300	-0.12274000
O	1.99037300	2.18422000	-0.91802300
O	0.84904900	0.12671900	0.85241900
O	-1.25018000	0.03590000	-1.13457200
La	-0.32764200	1.80892200	-0.01705000
O	-2.35991600	1.69178700	0.84977500
La	-3.22772500	-0.12201700	0.07865200
O	2.02981900	-1.78218000	-0.84355000
La	-0.09637100	-1.75615000	-0.13928200
O	-2.22830700	-1.81458400	0.77965900
C	4.81885400	-0.26268700	1.68429100
H	5.63293400	-0.95979500	1.39944300
H	4.40877200	-0.66427200	2.63296700
H	5.32135400	0.68725300	1.95934000
H	2.46103400	2.89919100	-1.35923900