ESI: ELECTRONIC SUPPLEMENTARY INFORMATION

Pyruvic acid proton and hydrogen transfer reactions in clusters

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I. CLUSTER REGION IN MASS SPECTRA

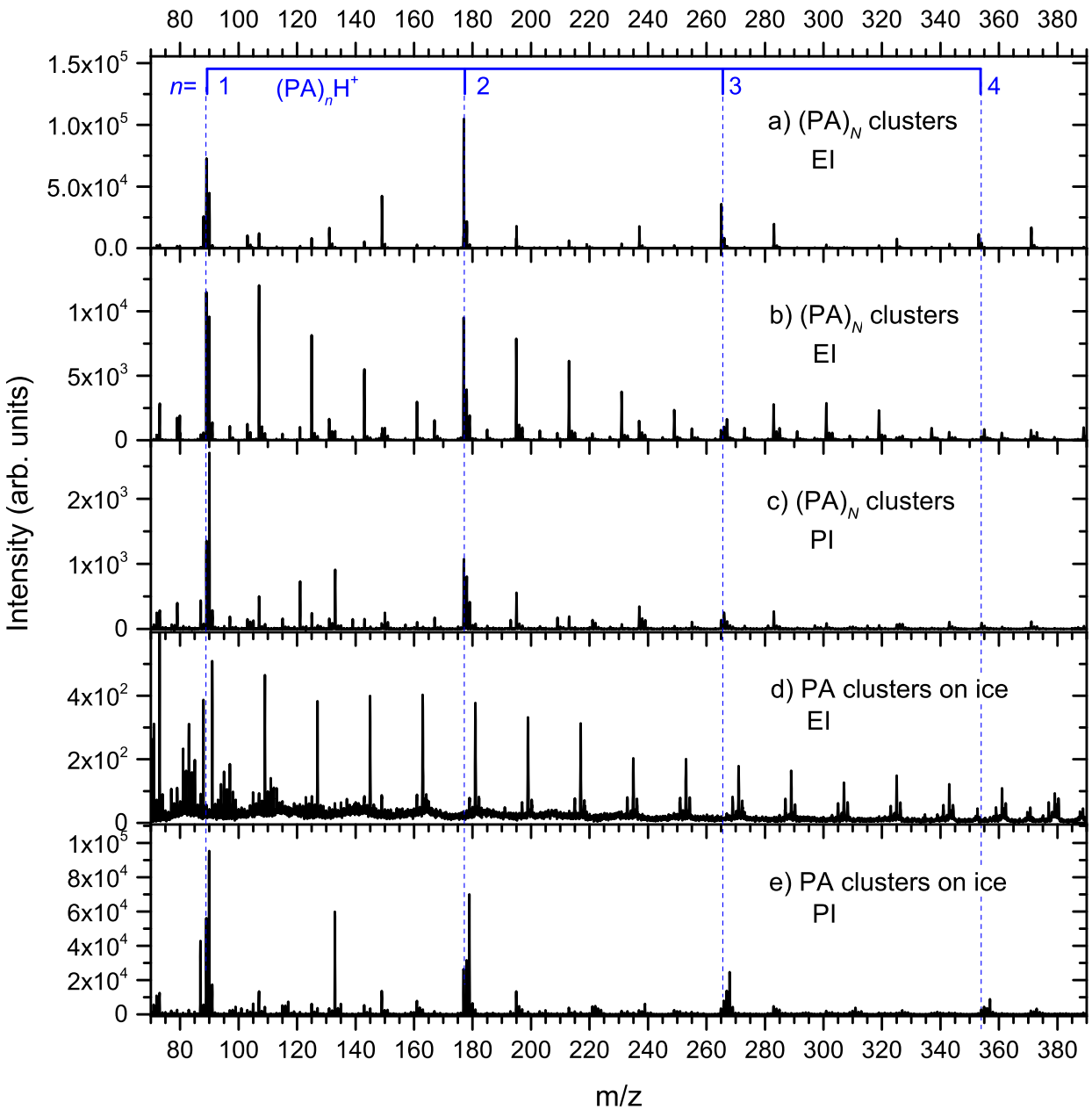

FIG. 1: Cluster region of mass spectra of isolated pyruvic acid clusters (a,b,c) and pyruvic acid clusters deposited on ice nanoparticles (d,e). Spectra (a,b,d) were recorded after electron impact ionization (70 eV electrons, EI) and the spectra (c,e) after multiphoton ionization (193 nm photons, PI). Spectrum (a) corresponds to the expansion of PA in He carrier gas, while spectrum (b) corresponds to expansion in Ar where some contamination with water is observed. Cluster series corresponding to protonated pyruvic acid clusters is indicated with a blue comb.

II. MOLECULAR FRAGMENTS

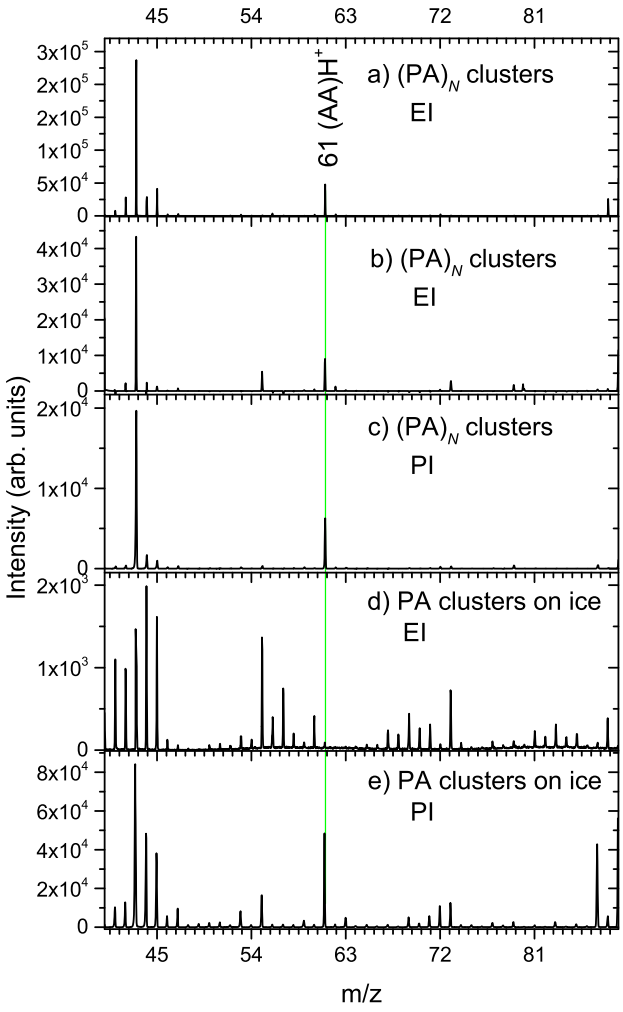

FIG. 2: Molecular region of mass spectra presented in figure 1. A peak at $m/z = 61$ is highlighted. This mass is not present in mass spectra of isolated PA molecules,[1] and it corresponds to a protonated acetic acid, $(AA)H^+$.

III. CARTESIAN COORDINATES (IN ANGSTROM) AND ELECTRONIC ENERGIES (IN HARTREE) OF THE STRUCTURES OPTIMIZED AT THE B3LYP+D2/DEF2TZVP LEVEL OF THEORY

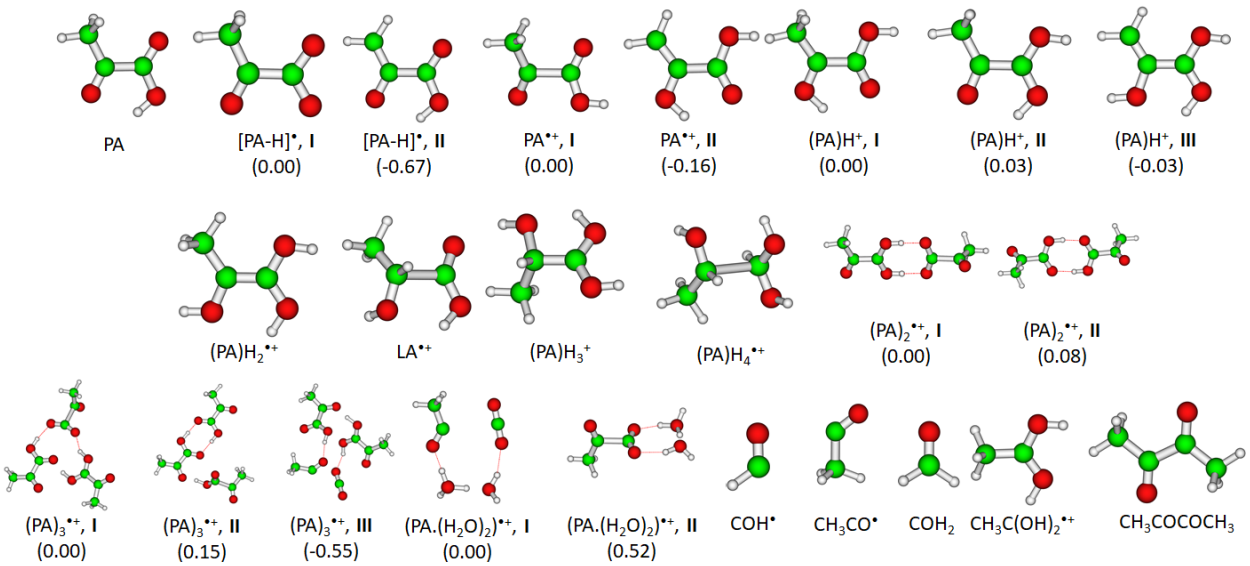

FIG. 3: Structures of molecules and ions optimized at the B3LYP+D2/def2TZVP level of theory. Relative energies are given in eV.

H2O

E=-76.441880

O 0.000000 0.000000 0.116876

H 0.000000 0.765219 -0.467505

H 0.000000 -0.765219 -0.467505

CO

E=-113.357483

C 0.000000 0.000000 -0.642794

O 0.000000 0.000000 0.482096

CO2

E=-188.658351

C 0.000000 0.000000 0.000000

O 0.000000 0.000000 1.159857

O 0.000000 0.000000 -1.159857

COH

E=-113.891299

C 0.061777 0.582496 0.000000

O 0.061777 -0.589441 0.000000

H -0.864878 1.220554 0.000000

COH2

E=-114.528319

C 0.000000 -0.526312 0.000000

O 0.000000 0.672928 0.000000

H -0.940782 -1.112770 0.000000

H 0.940788 -1.112781 0.000000

CH3CO

E=-153.207355

C -0.963915 -0.665213 0.000000

H -0.427770 -1.619624 0.000000

H -1.605758 -0.584136 0.879991

H -1.605758 -0.584136 -0.879991

C 0.000000 0.496344 0.000000

O 1.177847 0.475138 0.000000

CH3COCOCH3

E=-306.520855

C 1.890008 -0.564259 -0.000244

C 0.694743 0.346043 0.000046

C -0.694741 -0.346037 0.000084

C -1.890018 0.564259 -0.000207

O 0.757039 1.552188 0.000265

O -0.757028 -1.552184 0.000256

H 2.803186 0.028086 -0.000124

H 1.852419 -1.221055 0.872893

H 1.852394 -1.220600 -0.873722

H -2.803180 -0.028111 0.001161

H -1.851799 1.222096 0.872096

H -1.853065 1.219520 -0.874542

[PA-H], I

E=-341.816313

C 1.408503 1.260473 0.000000

C 0.000000 0.759102 0.000000

C -0.183189 -0.770397 0.000000

O -1.331394 -1.288010 0.000000

O -0.996547 1.430892 0.000000

O 0.748041 -1.590670 0.000000

H 1.933320 0.869101 0.877284

H 1.420672 2.349037 0.000000

H 1.933320 0.869101 -0.877284

[PA-H], II

E=-341.841088

C -1.675265 0.913139 0.000012

C -0.774547 -0.183803 -0.000006

O -1.137303 -1.360248 -0.000008

C 0.722670 0.183487 0.000025

O 1.126534 1.318541 0.000008

O 1.508487 -0.898283 0.000013

H -1.311618 1.930977 -0.000155

H -2.736357 0.702639 0.000037

H 2.429078 -0.590631 -0.000171

PA

E=-342.487803

c 1.354131 1.367029 0.000000

c 0.000000 0.737099 0.000000

o -1.050080 1.337588 0.000000

c -0.041539 -0.814625 0.000000

o 0.948088 -1.490147 0.000000

o -1.281497 -1.307301 0.000000

h 1.914365 1.021049 0.872924

h 1.262308 2.451298 0.000000

h 1.914365 1.021049 -0.872924

h -1.898679 -0.551536 0.000000

H2O+

E=-75.982077

O 0.000000 0.000000 0.115504

H 0.000000 0.826242 -0.462015

H 0.000000 -0.826242 -0.462015

H3O+

E=-76.703791

O 0.000040 -0.000004 -0.069610

H -0.500942 -0.804353 0.185600

H -0.446467 0.835815 0.185594

H 0.947086 -0.031433 0.185684

PA+, I

E=-342.132617

C -1.800659 0.754397 0.210273

C -0.811802 -0.330588 -0.031684

C 0.860525 0.250736 -0.020812

O 1.628293 -0.747463 0.253683

O -0.883555 -1.474242 -0.247400

O 1.000459 1.394931 -0.259336

H -1.601174 1.184235 1.197377

H -2.806676 0.341753 0.144422

H -1.616618 1.533553 -0.536742

H 2.574505 -0.492626 0.272709

PA+, II

E=-342.138435

C -1.519730 1.166921 -0.000026

C -0.734991 0.002640 0.000084

O -1.309313 -1.143160 -0.000006

C 0.793200 -0.055602 0.000022

O 1.340312 1.139896 -0.000008

O 1.308243 -1.137585 -0.000033

H -1.035927 2.135332 0.000128

H -2.601548 1.085887 -0.000239

H 2.314340 1.082852 -0.000029

H -0.621680 -1.861029 0.000040

[(PA)2]+, I

E=-684.664242

C 4.142629 1.167259 0.013980

C 3.440661 -0.150325 0.013696

C 1.870222 -0.095477 0.007131

O 1.269480 -1.203265 -0.098458

O 3.928207 -1.238637 0.021668

O 1.326795 1.049892 0.115154

O -1.297510 1.131388 0.115325

C -1.740987 0.012607 -0.036562

C -3.535412 0.076290 -0.193969

C -4.194425 -0.131311 1.127999

O -1.369274 -1.138109 -0.117871

O -3.905180 0.258224 -1.282924

H 3.847647 1.751209 -0.863321

H 5.216647 0.994663 0.011079

H 3.851800 1.748647 0.894076

H 0.257161 -1.201579 -0.101677

H 0.311424 1.101494 0.122209

H -5.275848 -0.084722 0.993820

H -3.881147 -1.104800 1.513948

H -3.843957 0.644886 1.813054

[(PA)2]+, II

E=-684.661311

C -4.155457 1.035438 0.456416

C -3.433160 -0.159482 -0.084859

O -3.888279 -1.120734 -0.611336

C -1.840123 -0.086580 0.011564

O -1.282802 0.825447 -0.560736

O -1.343102 -1.055484 0.694407

H -3.907997 1.147795 1.516700

H -5.227447 0.910264 0.316849

H -3.780918 1.917893 -0.071193

H -0.333427 -1.018051 0.704691

H 0.333458 1.018130 -0.704603

O 1.343125 1.055533 -0.694360

C 1.840129 0.086599 -0.011544

O 1.282783 -0.825409 0.560771

C 3.433158 0.159448 0.084843

O 3.888333 1.120771 0.611147

C 4.155404 -1.035542 -0.456341

H 5.227403 -0.910372 -0.316845

H 3.780879 -1.917935 0.071383

H 3.907887 -1.148014 -1.516600

(PA)H+, I

E=-342.781668

C -1.253418 -1.446755 0.000000

C 0.000000 -0.717341 0.000000

O 1.105762 -1.315109 0.000000

C 0.135659 0.821489 0.000000

O -1.028653 1.423081 0.000000

O 1.244854 1.275610 0.000000

H -1.842821 -1.113676 0.867136

H -1.107246 -2.524916 0.000000

H -1.842821 -1.113676 -0.867136

H -0.929236 2.394133 0.000000

H 1.852978 -0.654877 0.000000

(PA)H+, II

E=-342.780609

C -1.122173 -1.620896 0.000000

C 0.119283 -0.814831 0.000000

O 1.264182 -1.174077 0.000000

C 0.000000 0.746512 0.000000

O -1.136692 1.312954 0.000000

O 1.073003 1.419241 0.000000

H -1.726500 -1.370228 0.879038

H -0.868695 -2.679127 0.000000

H -1.726500 -1.370228 -0.879038

H 1.845545 0.795928 0.000000

H -1.110451 2.293998 0.000000

(PA)H+, III

E=-342.782785

C -1.412542 -1.255440 0.000231

C -0.760981 -0.088318 0.000083

C 0.693087 -0.018858 0.000070

O 1.300933 1.111369 0.000258

O -1.264798 1.172161 -0.000288

O 1.395078 -1.092100 -0.000311

H -0.863783 -2.186432 0.000290

H -2.494848 -1.296471 0.000300

H 0.665262 1.859094 0.000475

H -2.231026 1.193126 -0.000457

H 2.357314 -0.925051 -0.000177

[CH3C(OH)2]+

E=-229.431942

C 1.413334 -0.107764 -0.004633

C -0.057371 -0.006884 -0.011443

O -0.708546 1.100879 0.002932

O -0.742517 -1.082213 -0.002697

H 1.870052 0.758942 -0.484054

H 1.735017 -0.138808 1.045256

H 1.727442 -1.035674 -0.481932

H -0.148153 1.897611 -0.008752

H -1.711631 -0.943507 0.024054

[(PA)3]+, I

E=-1027.187740

C -4.929284 -1.583750 -0.882176

C -4.160792 -1.249971 0.348738

C -2.519259 -0.322037 -0.121888

O -2.818999 0.837094 -0.197272

O -4.310126 -1.405219 1.491806

O -1.676846 -1.168678 -0.206046

O 0.855194 -2.024792 -0.186359

C 2.029779 -1.554937 -0.029772

C 3.183026 -2.608962 -0.028640

C 4.557524 -2.068331 0.197243

O 2.337132 -0.343460 0.116177

O 2.875218 -3.749559 -0.209010

H -5.139426 -0.655479 -1.418144

H -5.851775 -2.096845 -0.604763

H -4.304234 -2.214731 -1.518361

H -1.728107 2.204969 -0.175786

H 0.080621 -1.402636 -0.181313

H 5.270381 -2.889528 0.173879

H 4.800418 -1.326636 -0.569289

H 4.602876 -1.548929 1.159166

O -0.992240 2.870728 -0.137190

C 0.156192 2.273270 -0.035058

O 0.283440 1.052496 0.008989

H 1.546762 0.357126 0.087519

C 1.399889 3.209087 0.027672

O 2.462864 2.653364 0.090829

C 1.169183 4.682954 0.004072

H 0.522983 4.970476 0.838955

H 2.123042 5.203000 0.060875

H 0.633810 4.959485 -0.909288

[(PA)3]+, II

E=-1027.182137

C 5.509749 -0.590259 0.111707

C 4.207877 -1.320328 -0.003914

O 4.069156 -2.509531 -0.069238

C 2.940075 -0.418488 -0.039039

O 3.025236 0.802253 0.031520

O 1.818200 -1.083228 -0.147358

O -0.262683 0.659787 -0.194318

C -0.062125 1.858651 -0.098063

C -1.273081 2.829141 -0.098361

O -2.390664 2.347292 -0.219276

O 1.075801 2.460006 0.009972

C -1.041976 4.281842 0.045562

O -3.057870 0.005240 -0.525778

C -2.802031 -0.799778 0.399472

C -3.365081 -2.397509 -0.097567

C -2.217122 -3.312791 -0.362858

O -2.304390 -0.833078 1.474919

O -4.525429 -2.514314 -0.117665

H 5.623929 0.101497 -0.727715

H 6.326613 -1.308405 0.129878

H 5.514003 0.021451 1.018266

H 1.049924 -0.457965 -0.165093

H 1.866328 1.793699 0.015050

H -1.983412 4.826039 0.027298

H -0.495054 4.465610 0.976656

H -0.373953 4.616957 -0.755183

H -2.666508 1.023254 -0.367176

H -2.599086 -4.267253 -0.724888

H -1.547723 -2.846323 -1.089542

H -1.671631 -3.426873 0.578592

[(PA)3]+, III

E=-1027.208215

C 0.369561 -1.833260 0.169986

O 0.328589 -0.785200 0.904123

O -0.670199 -2.435247 -0.161905

C 1.747530 -2.352121 -0.331968

O 2.691042 -1.659820 -0.059395

C 1.753911 -3.627338 -1.096915

H 2.772941 -3.872640 -1.387833

H 1.111716 -3.532183 -1.977950

H 1.323405 -4.427119 -0.485847

H -1.632688 -1.973963 0.114308

O -2.880683 -1.560772 0.448567

C -3.310226 -0.419967 0.316221

C -2.380083 0.688215 -0.210115

O -1.522632 0.228003 -1.109076

O -2.445011 1.805937 0.223065

C -4.678068 -0.024581 0.710570

H -5.205823 0.345500 -0.176767

H -4.615653 0.826119 1.395767

H -5.212993 -0.861674 1.153334

H -0.826156 0.909681 -1.283093

H 1.217226 -0.362561 1.054747

O 2.410189 0.849883 1.516015

C 3.404125 1.109594 0.957584

O 4.381801 1.376479 0.415339

C 0.946588 2.889512 -0.749411

O 0.705218 1.768021 -1.059586

C 0.060653 4.084728 -0.662147

H -0.990909 3.783378 -0.637414

H 0.322546 4.677639 0.214961

H 0.265911 4.700856 -1.544209

[(PA)H2]+

E=-343.378215

C -1.658078 -1.018254 0.000037

C -0.676050 0.086490 0.000073

C 0.731162 -0.077222 0.000123

O 1.578083 0.914578 0.000064

O -1.044468 1.360605 -0.000265

O 1.222336 -1.281375 -0.000131

H -2.299158 -0.944586 0.886271

H -2.300021 -0.943592 -0.885469

H -1.165207 -1.987752 -0.000669

H 1.145356 1.787100 0.000245

H -2.007485 1.478319 0.000842

H 2.196700 -1.286027 0.000039

LA+

E=-343.326019

C 1.659451 0.959133 -0.171626

C 0.830760 -0.133555 0.407112

C -0.998724 0.233830 0.017087

O -1.691798 -0.839505 -0.110248

O 0.995538 -1.390208 -0.022530

O -1.248591 1.376757 -0.013006

H 1.665688 0.929789 -1.264699

H 2.685521 0.816236 0.189132

H 1.302350 1.931850 0.162847

H -1.154218 -1.653571 -0.048279

H 1.469255 -1.434494 -0.872249

H 0.641301 -0.122608 1.484083

[(PA)H3]+

E=-343.991483

C 1.378817 -1.182085 0.431096

C 0.694097 -0.112074 -0.426079

O 1.183433 1.200049 -0.227826

C -0.759639 0.006078 -0.067215

O -1.530400 -0.993157 -0.254446

O -1.214121 1.085763 0.425909

H 1.317262 -0.926075 1.490280

H 2.426857 -1.238385 0.132814

H 0.921575 -2.157010 0.260062

H -0.465827 1.737382 0.475084

H 2.132446 1.201854 -0.054203

H 0.736575 -0.396845 -1.485534

H -2.459828 -0.833678 0.005595

[(PA)H4]+

E=-344.530601

C -1.672775 1.125253 0.097490

C -0.979207 -0.082433 -0.411133

C 1.023842 0.057959 0.381844

O 1.600128 -1.020715 -0.107960

O -1.344008 -1.298059 -0.010160

O 1.484872 1.208978 -0.038084

H -1.878327 1.051471 1.169561

H -2.631920 1.227994 -0.427441

H -1.085235 2.021593 -0.101471

H 1.240475 -1.838578 0.271024

H -1.944665 -1.268784 0.752404

H -0.574546 -0.099058 -1.419189

H 2.081623 1.113016 -0.802097

H 0.633492 0.066037 1.397643

[PA.(H2O)2]+, I

E=-495.110580

C -2.660251 -1.471237 0.119120

C -1.195720 -1.234928 0.079300

O -0.292128 -1.997471 -0.068127

C -0.853891 2.035417 -0.055331

O -2.004532 2.025038 -0.120156

O 0.309485 2.041240 0.009069

O 2.861314 0.792090 0.075579

H -3.021074 -1.181720 1.110976

H -2.892649 -2.519767 -0.087916

H -3.144887 -0.805097 -0.598907

H 2.120948 1.422854 0.064152

H 2.544790 -0.514105 0.012725

H 3.534951 1.103001 0.694597

O 2.267787 -1.571663 -0.050087

H 2.711415 -2.053767 -0.764086

H 1.270273 -1.740789 -0.060301

[PA.(H2O)2]+, II

E=-495.091511

C 2.818789 0.119609 -1.081608

C 2.121596 -0.011716 0.228468

O 2.449251 -0.120553 1.338956

C 0.268971 0.019795 -0.013620

O -0.082922 1.167481 -0.016427

O -0.104054 -1.130110 -0.102462

O -2.719346 -1.235477 -0.175242

H 2.497226 -0.700046 -1.728540

H 3.896764 0.092555 -0.915427

H 2.511030 1.063276 -1.538303

H -1.724714 -1.391328 -0.159199

H -2.893942 -0.147663 -0.044079

H -3.171979 -1.796282 0.473825

O -2.899798 1.171741 0.128070

H -2.000007 1.550329 0.084880

H -3.515560 1.738384 -0.355753

[1] *NIST Mass Spec Data Center, S.E. Stein, director, "Mass Spectra" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, ed. P. J. Linstrom and W. G. Mallard, National Institute of standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov), June 2005.