B3LYP/6-311++G(2d,p) // B3LYP/6-31G(d)

Frequencies in cm^{-1}, zero-point kinetic energies (ZKEs) and energies (Es) in Hartrees. The energies are not corrected for ZKE.

AP^{+}(CE) parent ion:

Charge: 1+; Spin state: Singlet

Geometry:

O,0,-3.7777505407,2.2169901773,-1.0375091942

N,0,0.769381306,-0.0312046221,-0.1332981201

C,0,-0.4294078135,-0.0351291735,-1.0334968604

C,0,-1.2827139434,-1.260649809,-0.6621897452

O,0,-0.7369117855,-2.2651943861,-0.20885728

C,0,0.0289097687,-0.1026917361,-2.4956820704

C,0,-3.4754569066,-2.3603068562,-0.5902160702

N,0,-2.6166951519,-1.1934230509,-0.8916361204

C,0,-3.3648661457,-0.0763354848,-1.4713812081

C,0,-3.6793875811,1.0095931453,-0.4411381001

O,0,-3.8688742907,0.8261135615,0.7398864644

C,0,-4.6796247724,-0.75406666,-1.936951223

C,0,-4.8945321351,-1.8563698386,-0.8873426252

H,0,-4.0599134806,2.8539923021,-0.3529243365

H,0,1.2057965976,0.906486519,-0.1422968926

H,0,0.5171955697,-0.254649512,0.8499583025

H,0,1.4782132236,-0.7210199922,-0.4417009903

H,0,-0.9572794428,0.8964667095,-0.8237398675

H,0,0.7347687689,0.7027772991,-2.7174338707

H,0,-0.823071069,-0.013755916,-3.175183872

H,0,0.5206710449,-1.0618411288,-2.6846606747

H,0,-3.1821827816,-3.1990442851,-1.2315592718

H,0,-3.3309927434,-2.6682847464,0.4480559726

H,0,-2.8378207081,0.3797586072,-2.312171219

H,0,-4.5142500975,-1.185483779,-2.929980475

H,0,-5.5089317486,-0.0457613774,-2.011653475

H,0,-5.5483346809,-2.6540590097,-1.2484207509

H,0,-5.3416652296,-1.4334709284,0.0171539316

O,0,1.5747433394,2.8234625532,0.1181947365

C,0,2.3521495638,3.3801917356,-0.9397912099

C,0,3.5758405661,2.5153822924,-1.1546520909

O,0,3.1600127266,1.2307708949,-1.5931876064

H,0,2.6756482835,4.3970727932,-0.6733071136

H,0,1.758076147,3.4422239044,-1.8640809533

H,0,4.2244970104,2.9915910316,-1.9066210777

H,0,4.1438939944,2.4365581405,-0.2151410505

C,0,-1.3366432756,1.2779182708,2.692695878

O,0,-0.7595601622,1.9082742374,1.5464389043

O,0,0.0961433957,-0.6384082176,2.6255470586

C,0,-0.3451825066,0.4234319871,3.4658108372

H,0,-2.1471709427,0.6529266051,2.3124601286

H,0,-1.7720440557,2.0308054848,3.3656808333

H,0,0.5167110602,1.0111940873,3.817886771

H,0,-0.8514934611,0.013283438,4.3531065852

C,0,3.5796953201,-2.5823006283,-0.5177702853

O,0,2.8740601318,-1.6618890529,-1.3558860888

O,0,2.1981803496,-2.2077875441,1.387347049

C,0,2.6046298125,-3.2030508185,0.4589727647

H,0,4.3805506353,-2.0712595306,0.0343856944

H,0,4.0309625325,-3.3700710763,-1.1377963405

H,0,1.7355762681,-3.6047543698,-0.0806388607

H,0,3.1069270818,-4.0339729896,0.97995178

C,0,0.5130666812,3.6729196698,0.5491249747

H,0,0.9021386109,4.6828335824,0.7448924423

H,0,-0.2618345831,3.7498136304,-0.2287383761

C,0,-0.0798828434,3.122863834,1.8293072583

H,0,0.7268896914,2.9718871566,2.5607747015

H,0,-0.7813465104,3.863264042,2.2452222524

C,0,0.915230902,-1.5901849772,3.3066457298

H,0,0.3582957852,-2.0088448729,4.1576778879

H,0,1.821948772,-1.1024176471,3.6943476497

C,0,1.2909901526,-2.7104868572,2.361017164

H,0,1.767398638,-3.5151303342,2.943863165

H,0,0.3913765155,-3.1108855765,1.8764603259

C,0,3.6926067695,-0.9856711572,-2.3112249113

H,0,4.520459912,-1.6344905883,-2.6266236467

H,0,3.0609798443,-0.7951917998,-3.184316474

C,0,4.2451908256,0.3338512206,-1.7976213507

H,0,4.9449504413,0.743627837,-2.5436665095

H,0,4.8037835454,0.1910239973,-0.8592694765

Vibrational frequencies:

17.4791	31.2641	36.6658
40.2301	43.1958	50.9659
63.5361	74.5116	79.7512
88.4023	94.8508	99.7383
106.4700	117.5367	127.4217
131.9619	137.1096	141.7034
145.6297	157.7989	163.0418
166.3531	174.6095	188.4218
208.7899	226.9394	232.1257

240.1993	259.2097	266.2393
266.6630	268.4359	285.6821
298.8309	305.0806	314.1401
317.4600	326.4458	331.9337
347.0895	358.8580	386.3335
396.0703	399.6450	414.4945
465.8787	513.0385	518.6406
528.8829	540.8922	550.9391
578.0880	580.2712	582.0510
636.3722	651.5916	719.4135
744.4153	769.3111	823.1689
829.4266	833.9207	843.2669
854.4799	856.9737	858.4007
876.1191	885.4878	897.5102
922.8784	924.7279	931.7408
948.1482	953.1285	964.3653
973.4813	977.5652	983.0621
1000.7287	1020.5836	1039.4475
1059.5575	1060.4150	1072.6704
1078.5613	1089.1202	1103.8894
1109.7245	1115.8516	1123.2965
1124.2076	1130.0294	1133.8520
1139.2867	1143.1562	1148.5482
1158.1742	1160.7499	1167.3825
1169.5501	1172.9099	1175.4325
1178.1260	1194.2151	1201.0006
1213.7885	1225.3686	1258.5820
1268.0068	1269.1970	1271.3072
1275.9864	1280.4207	1284.9347

1288.2570	1303.6918	1310.1587
1317.8055	1322.5000	1323.4081
1330.5057	1341.0124	1344.6186
1346.5267	1354.6782	1377.2206
1390.0095	1394.5033	1399.1747
1401.6794	1403.7008	1415.7355
1425.2966	1428.6353	1434.9013
1444.0635	1445.0010	1448.0913
1464.6162	1465.9255	1480.5743
1483.8863	1488.7184	1512.6143
1518.1526	1518.9018	1522.3471
1523.0562	1524.0193	1524.4276
1525.4560	1526.0018	1534.6378
1535.6768	1541.2792	1543.4519
1546.4884	1546.7062	1548.0753
1548.8924	1635.2320	1691.4692
1704.5690	1756.5819	1845.6650
3000.3978	3004.4254	3006.0519
3008.4323	3009.1115	3009.9251
3013.6026	3019.0219	3021.2128
3026.8866	3037.1900	3037.3297
3045.5315	3046.1043	3051.3244
3054.4430	3058.0050	3060.3327
3060.8627	3062.7161	3073.4126
3073.9976	3075.5162	3081.3402
3084.0491	3094.0548	3119.7254
3122.0512	3129.9529	3134.9438
3136.3108	3148.3455	3153.5666
3154.9574	3155.0993	3223.0496

3287.1357 3325.5298 3677.8590

ZKE = 0.619656

E = -1572.4237424

AP^{+} fragment:

Charge: 1+; Spin state: Singlet

Geometry:

O,0,-4.4326621946,1.7956315918,-0.4268366282

N,0,0.2475707284,0.3048690568,-0.0634067724

C,0,-0.3939039547,-0.0137040682,-1.4027704742

C,0,-1.2873279717,-1.2225673776,-1.0369845533

O,0,-0.7105577411,-2.1640827544,-0.4908069575

C,0,0.6703228886,-0.3899880716,-2.4286312735

C,0,-3.44403844,-2.382880017,-0.982830451

N,0,-2.6053758996,-1.1978724299,-1.3134635055

C,0,-3.4217032633,-0.0133869155,-1.6141841617

C,0,-3.3732901724,0.9913629509,-0.4457323749

O,0,-2.448444099,1.0882174542,0.3461592626

C,0,-4.8167010026,-0.6133685159,-1.8900867706

C,0,-4.8716826271,-1.8240182657,-0.9455105135

H,0,-4.3260072682,2.4380335546,0.3032462698

H,0,1.0497103333,0.9389377971,-0.1317102822

H,0,-0.4874557632,0.7147905025,0.5379951689

H,0,0.5413408094,-0.6017696894,0.3389314712

H,0,-0.9373579932,0.882250153,-1.6960548712

H,0,1.3734876735,0.433721054,-2.5936914823

H,0,0.187069631,-0.608170518,-3.38570293

H,0,1.2148599489,-1.284727447,-2.1146436565

H,0,-3.3100582425,-3.1356011002,-1.7667441825

H,0,-3.1083049136,-2.8158549604,-0.0385537895

H,0,-3.0508938033,0.5234409975,-2.4966220431

H,0,-4.8537795887,-0.9367613677,-2.9352784233

H,0,-5.6150104215,0.1118164811,-1.7298058636

H,0,-5.610733778,-2.5653214067,-1.2573885285

H,0,-5.131690875,-1.5043926882,0.0703343164

Vibrational frequencies:

50.0771	75.6360	101.9159
110.1735	135.9395	179.8911
186.7758	251.8846	268.4306
292.3670	314.8364	329.2706
364.3288	380.6325	429.4913
445.3428	523.4299	562.7744
601.8740	662.0795	703.6824
727.5211	755.5183	818.0182
844.6931	873.9164	882.0628
919.6475	933.8416	950.2725
981.1828	988.8824	1014.3700
1068.8409	1096.6800	1119.6135
1131.7353	1188.6642	1196.1039
1210.7008	1224.6005	1238.2779
1278.4580	1298.4957	1337.4628
1346.3931	1355.6940	1374.1980
1385.2967	1396.1251	1417.5864
1441.7352	1474.5921	1486.3093
1513.5911	1520.5664	1527.3375

1529.7767	1546.1147	1645.5824
1713.6608	1757.3016	1795.2104
3060.3857	3068.7592	3073.4669
3085.9557	3095.4003	3141.4371
3143.5682	3151.8334	3157.1864
3172.4537	3180.3607	3306.5145
3370.0209	3497.4214	3661.2954

ZKE = 0.244774

E = -649.0757382

CE fragment:

Charge: zero; Spin multiplicity: Singlet

Geometry:

O,0,1.7536760266,2.9356934257,0.3657942712

C,0,2.4326489431,3.383646027,-0.7875328671

C,0,3.6254454553,2.4839461745,-1.0486782896

O,0,3.1767481285,1.2449811881,-1.5542689221

H,0,2.7891060354,4.4210100312,-0.6508032888

H,0,1.7679077979,3.3709360653,-1.6664354261

H,0,4.2977810599,2.9788265593,-1.7730254473

H,0,4.1873649467,2.3465585533,-0.1103472976

C,0,-1.4178047184,1.2425898438,2.5452253721

O,0,-0.7580984229,1.9100055546,1.4868543442

O,0,-0.0872350065,-0.7412415801,2.6378071498

C,0,-0.5092056884,0.3671073615,3.4014234941

H,0,-2.1728481988,0.6025383202,2.0769156199

H,0,-1.9371866481,1.9646964991,3.1989865319

H,0,0.3592377842,0.9414554302,3.7652223705

H,0,-1.0753873349,0.0361410563,4.292430529

C,0,3.5926887189,-2.4801505729,-0.4119690048

O,0,2.8455201912,-1.6944784661,-1.318850405

O,0,2.1896120077,-2.1871304564,1.4998397481

C,0,2.6437933181,-3.1445636422,0.5671817826

H,0,4.318478159,-1.8770146928,0.1546817426

H,0,4.1553806702,-3.2604944145,-0.9553863812

H,0,1.8005729323,-3.5859928646,0.0119593566

H,0,3.1752977566,-3.9658478893,1.0819549161

C,0,0.5971921612,3.6914050696,0.6560105625

H,0,0.8644240913,4.7421059299,0.8718931262

H,0,-0.0996810901,3.6904647255,-0.1975198797

C,0,-0.0973013558,3.100015821,1.8678420078

H,0,0.6539915559,2.9210832586,2.6521752669

H,0,-0.8251457471,3.8329100425,2.2602799962

C,0,0.7838020657,-1.6010369136,3.3406783132

H,0,0.2690492314,-2.0504119755,4.2094113955

H,0,1.6605293877,-1.0504379633,3.7192092503

C,0,1.2523653325,-2.7089850103,2.4169365902

H,0,1.7078441401,-3.5129906837,3.0235716968

H,0,0.3830874758,-3.1370426239,1.8919134494

C,0,3.626889032,-0.992286224,-2.2660528298

H,0,4.4445681304,-1.6286966559,-2.6468137911

H,0,2.9572735623,-0.7618668663,-3.1012716617

C,0,4.2188174768,0.3146112145,-1.7495492256

H,0,4.945839291,0.6912964201,-2.4935553909

H,0,4.7732773455,0.1496619235,-0.8105207752

Vibrational frequencies:

34.0640	37.2238	51.4173
57.9214	71.4459	97.3413
128.5194	128.7727	145.2496
146.2132	154.6355	168.4576
191.8658	204.9853	220.0933
223.6937	257.0172	286.5672
301.8034	302.8370	320.5183
352.1493	389.0786	393.2067
506.1469	510.8512	536.5080
552.8672	585.3018	587.8197
837.6307	845.8303	859.4954
859.8586	867.9475	878.2624
921.1144	945.3369	958.4547
966.7630	976.9719	979.2194
1069.4363	1077.2460	1085.8246
1092.3508	1108.2722	1112.9806
1118.6861	1133.1380	1148.4950
1149.2621	1165.6084	1171.3235
1173.9742	1176.5698	1186.2346
1188.9184	1196.4792	1196.7725
1265.5029	1265.6799	1276.7634
1277.3519	1284.2087	1285.6685
1313.6859	1318.0827	1320.9065
1324.7081	1344.6725	1344.7598
1389.3450	1400.6921	1403.5202
1415.8947	1423.2964	1431.7929
1443.7486	1446.1642	1463.8228
1465.4799	1483.6655	1484.3198

1507.5668	1507.5761	1522.2907
1522.8422	1524.5141	1524.7248
1537.8458	1537.9600	1550.3165
1550.5638	1551.8046	1552.3288
2951.3401	2951.4184	2955.6618
2955.6958	2959.9496	2960.1192
2972.3583	2973.0242	2977.4118
2977.5037	2987.2299	2988.4509
3002.3837	3002.4974	3008.3829
3008.4740	3016.3830	3016.4469
3023.8028	3024.1067	3035.3363
3035.7212	3104.9230	3104.9272

ZKE = 0.370545

E = -923.2754226

a^+(CE) fragment:

Charge: 1+; Spin state: Doublet

Geometry:

N,0,0.8454138513,0.0998872768,-0.1107901752
C,0,-0.3032837212,0.0442326118,-1.0114512797
C,0,-0.0736258649,-0.2773504694,-2.4409095408
H,0,1.2189012894,1.0724356054,-0.0307349334
H,0,0.5795812939,-0.1932192746,0.8509910992
H,0,1.6183370692,-0.5104121084,-0.4387273718
H,0,-1.1636842223,0.5878961238,-0.6443436352
H,0,0.5161352946,0.5053003956,-2.9482396249
H,0,-1.0280407805,-0.3672690524,-2.9660935559

H,0,0.4790903511,-1.2183894045,-2.5578959466

O,0,1.6829903233,2.8573493272,0.2556105746

C,0,2.4768112568,3.4060451789,-0.7981796336

C,0,3.6814449186,2.5183546991,-1.0276549435

O,0,3.2412360495,1.2561417858,-1.5077512343

H,0,2.8220005962,4.4113434222,-0.5173379498

H,0,1.8831123921,3.4911935868,-1.7200659074

H,0,4.3448817629,3.0025509361,-1.7610378348

H,0,4.2417767402,2.3993282877,-0.0875880609

C,0,-1.4362167904,1.2880224985,2.5640312418

O,0,-0.7434413575,1.9392498219,1.5030597398

O,0,-0.0469513493,-0.6691637046,2.561669779

C,0,-0.5418538106,0.3795461447,3.3937375559

H,0,-2.2194560637,0.687286716,2.0913283988

H,0,-1.9199463713,2.0235424884,3.2227281459

H,0,0.2974598315,0.9367436672,3.8370130283

H,0,-1.1323845318,-0.0462968401,4.2188668585

C,0,3.6269162965,-2.4845624797,-0.4020144881

O,0,2.9073920268,-1.613583733,-1.278704323

O,0,2.0914369105,-2.1819035855,1.3979197208

C,0,2.646124757,-3.1614067509,0.5316525103

H,0,4.3688852074,-1.9253914124,0.1840568895

H,0,4.1524380161,-3.2485756891,-0.9920072822

H,0,1.8560854437,-3.6602794018,-0.0506815114

H,0,3.1795279858,-3.9313991093,1.1106728821

C,0,0.6119834973,3.7151101206,0.6555020906

H,0,1.0107542815,4.7081179674,0.9080013666

H,0,-0.1125915901,3.8323851838,-0.1632829644

C,0,-0.0680923041,3.1341017838,1.8775231001

H,0,0.6846495887,2.9430976172,2.6559813493

H,0,-0.7864096961,3.870380216,2.2691259962

C,0,0.7348812473,-1.6231169456,3.2816794726

H,0,0.1319042455,-2.0608638768,4.0903494399

H,0,1.6117722106,-1.133768611,3.7301514628

C,0,1.1817675816,-2.7245825389,2.3446746215

H,0,1.6678727399,-3.5147743627,2.9378118543

H,0,0.3105598505,-3.1681033413,1.8382568434

C,0,3.7166401573,-0.9558592198,-2.2597915256

H,0,4.519217883,-1.6255486897,-2.5956378535

H,0,3.0598226716,-0.7559364454,-3.1112928378

C,0,4.3084334963,0.3532982137,-1.7638540517

H,0,4.9806999514,0.7580394624,-2.5372890217

H,0,4.907111387,0.1985759085,-0.8522135347

Vibrational frequencies:

34.2900	40.0108	41.8034
65.9526	86.4107	91.2162
98.3987	104.3950	108.9270
134.4268	137.9801	146.5883
147.6308	152.4915	159.5467
163.6576	172.2379	202.1362
215.3365	230.1211	237.1464
250.5024	266.9939	271.0762
299.0097	306.6872	317.2826
324.5353	343.7868	385.5880
397.5950	421.7502	475.2332
503.1106	511.8157	517.4414
542.4285	550.8638	577.8511

579.6380	821.2465	831.9410
841.8284	852.3684	855.0597
885.6439	902.0275	924.3333
946.2394	950.8353	963.4679
976.6561	980.7504	1006.2591
1040.1324	1057.9043	1071.1396
1075.6121	1086.4079	1103.3924
1107.3921	1115.6350	1121.5285
1130.0223	1132.0750	1135.9051
1148.5687	1156.0324	1156.7064
1161.0992	1168.2511	1172.6381
1174.0064	1176.4049	1187.5311
1244.7007	1267.4146	1268.9217
1276.9759	1277.6398	1283.0828
1286.6588	1309.5730	1316.9884
1322.1483	1329.8249	1342.4851
1344.1419	1389.5843	1400.1210
1402.6796	1408.5421	1416.1224
1423.5208	1431.5500	1443.5045
1446.0102	1450.5864	1463.5639
1465.3188	1484.2121	1484.5199
1494.0765	1505.5192	1510.1045
1516.9306	1522.8497	1523.4190
1525.5215	1526.0016	1534.7069
1537.6391	1544.4674	1546.3031
1547.8286	1548.7719	1639.4525
1685.9245	1716.2262	2991.0406
3000.7415	3004.7422	3010.7086
3010.9822	3011.9591	3016.0656

3021.3214	3022.9044	3026.2923
3028.8950	3036.3589	3039.3513
3045.9026	3048.1297	3049.0476
3051.7914	3057.0808	3057.4100
3067.0694	3068.1814	3071.3305
3073.1958	3077.6073	3117.7653
3126.7137	3137.1121	3147.5800
3210.0225	3248.6738	3268.0927

ZKE = 0.468348

E = -1058.2821788

x fragment:

Charge: zero; Spin state: Doublet

Geometry:

O,0,-3.8648152692,2.1754777755,-1.1335294367
C,0,-1.3108358516,-1.1985106434,-0.673992899
O,0,-0.6412246324,-2.0645652416,-0.1667490139
C,0,-3.5060985676,-2.375641117,-0.7061999806
N,0,-2.6125826219,-1.2271558461,-0.9943366361
C,0,-3.3137908367,-0.0899755933,-1.5763615484
C,0,-3.6074606928,0.9885289531,-0.5324311902
O,0,-3.653450918,0.8239718459,0.6637317174
C,0,-4.6304500549,-0.7271225317,-2.0823631579
C,0,-4.9026529236,-1.8331821123,-1.0446598244
H,0,-4.0791799382,2.8055383072,-0.4194814243
H,0,-3.2210533534,-3.2240426488,-1.3397357869

H,0,-3.39875606,-2.6774186281,0.3390312781

H,0,-2.7333025764,0.359207477,-2.3863289349

H,0,-4.4540707859,-1.1592872784,-3.0735643891

H,0,-5.441038625,0.0009889853,-2.1705695422

H,0,-5.5695442292,-2.6113850775,-1.4267330956

H,0,-5.3620660632,-1.4016056258,-0.1497071353

Vibrational frequencies:

37.0529	48.4760	89.3670
156.2785	204.9685	264.2020
315.9214	376.1215	410.0339
507.5077	571.5472	617.3711
646.3068	742.7139	767.6182
824.2551	869.0836	890.8081
925.4737	925.9736	990.5302
1047.4514	1122.4664	1161.9157
1180.9950	1198.1930	1221.8282
1265.7223	1290.2852	1319.1596
1336.8981	1352.8335	1373.0664
1392.7900	1425.0993	1520.2416
1526.2227	1546.7296	1837.7843
1856.9831	3061.3921	3076.2200
3083.2919	3112.4219	3119.9156
3129.9866	3139.1050	3683.2572

ZKE = 0.142531

E = -514.0117667

Supplementary info on rate constants

March 16, 2017

The calculation of the rate constants is made with the detailed balance formalism. As a reference we give the expression for evaporation of a single atom. It reads [V. Weisskopf, Phys. Rev. vol 52, 295 (1937).]

$$k(E,\varepsilon)d\varepsilon = \frac{mg\sigma\varepsilon}{\pi^2\hbar^3}\frac{\rho_p(E-\Delta E-\varepsilon)}{\rho_r(E)}d\varepsilon, \tag{1}$$

where ε is the kinetic energy release, m the reduced mass of the channel, g the degeneracy of the electronic state of the atom. The degeneracies for the reactant and the largest product are included in the vibrational level densities, ρ_r and ρ_p respectively. σ is the capture cross section for the inverse process and ΔE is the activation energy for the evaporation process.

This is a well known result from nuclear physics where it was used by Weisskopf to describe decay of excited nuclei by neutron emission, and has also been used in the quantitative description of cluster decay, by emission of atoms, electrons and, with some modifications, also photons.

To convert Eq. 1 to one applicable to evaporative separation of larger fragments, we first make the simple change and include g into the relevant level density. Numerically this is minor change. Secondly we calculate the vibrational product level density as the convolution of the vibrational level densities of the two products, denoted by the subscripts $p1$ and $p2$:

$$\rho_p(E) = \int_0^E \rho_{p1}(x)\rho_{p2}(E-x)\mathrm{d}x \tag{2}$$

This is easily implemented by pooling the vibrational degrees of freedom of both products. This and all other calculations of vibrational level densities was done with the Beyer-Swinehart algorithm, as mentioned in the main text.

We now address the questions of the rotational degrees of freedom and of the magnitude of the capture cross section. These two are both related to the transition state. For all channels considered here, the products will consist of one cation and one neutral molecule. The interaction between the neutral product and the ion has a strength which is larger than the relevant collision energies, which are on the order of the thermal energies of the products. This makes the formation of a bound complex in the reverse process collisions very likely, also in the cases where the attachment reaction does not immediately proceeds to the end with the resulting formation of the intact peptide. The formation of the parent ion in the reverse process from the formed complex then proceeds in competition with the statistical re-decay of the complex. We expect that geometric rearrangements have lower energy barriers than dissociation and that a complex-forming collision therefore will yield the parent ion with a considerably higher probability than given by considerations of steric factors and with values closer to the geometric cross sections.

Another effect that should be considered in the evaluation of the rate constant is the increased capture cross section due to the charge, on one fragment, and the dipole moment and the polarizability of the other, neutral fragment. This will increase the capture cross section compared to the purely geometric value, and thus introduce an approximation in the opposite direction of the one made by ignoring the re-evaporation discussed above. Both approximations will potentially change the rate constant by only a couple of orders of magnitude, and the fact that they have opposite effect means that we can use the geometric cross section to a reasonable accuracy.

What remains is to include the rotational degrees of freedom into the rate constant. Some theory is available in the literature but it still requires a not insignificant amount of theoretical development. The problem arises by the presence of three angular momenta after the decay; an intrinsic rotation for each of the fragments and one orbital angular momentum. The orbital angular momentum is related to the capture cross section and the translational kinetic energy release and need no further consideration. The other two are the angular momenta associated with the rotational motion of the isolated fragments (we ignore spin in this connection).

We expect these will have little influence on the branching ratio. This follows from considerations of the possible limiting cases of the theory of the rate constants that include the angular momenta. Two extreme cases must bracket the exact value. One extreme is the complete absence of any effect of the rotations. The first limit corresponds to multiplication of the ratio of level densities with the trivial factor unity squared and has no effect. The other is a multiplication of the level densities with the canonical rotational partition functions of the two freely rotating fragments, calculated at the product temperature. This follows from a freely populated rotational manifold during the break-up process. The convolution of the rotational and vibrational level densities yields the rotational partition function as a multiplicative factor. For details see my book. This can amount to a significant correction for individual rate constants. However, when one takes the ratio of two different rate constants that involve fragments of similar size, mass, and disintegration energy, these factors tend to cancel. This is so because the moments of inertia of the fragments are similar, and the similar value of the (microcanonical) temperature in the two processes. In both limits, the angular momenta corrections to the rate constants therefore cancels at least approximately and we therefore expect that we can calculate the ratios of the rate constants with good confidence by simply ignoring any angular momentum correction to the rate constants themselves.

Similarly, the remaning parts of the frequency factors, given by Eq. 1 are similar in the same cases. The branching ratio, B, is then simply given by the ratio of product vibrational level densities, i.e.

$$B_{1,2} \approx \frac{\rho_1(E-\Delta E_1)}{\rho_2(E-\Delta E_2)}, \tag{3}$$

where the subscripts refer to the channel considered.

A numerical example of the rate constant for crown ether loss is shown in the main text. The factor on the atomic evaporation rate constant is arbitrarily set to 10^6. In a classical treatment of the fragment rotational partition functions this corresponds to the product of all six principal axes rotational partition functions;

$$Z_{1,2}^{rot} = \left(\frac{T^6}{T_{1,x}T_{1,y}T_{1,z}T_{2,x}T_{2,y}T_{2,z}}\right)^{1/2}, \tag{4}$$

where $T_{i,x}$ is the rotational constants (in units of temperature) of the first principal axis of fragment i etc., and T is the product microcanonical temperature. The factor 10^6 then corresponds to a geometric average of $T/T_{i,x} = 100$. For comparison is the rotational constant of C_2 equal to 5 K.