

Electronic Supplementary Information

The structures of cationic gold clusters probed by far-infrared spectroscopy

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1. Calculated Ar adsorption energies

Table S1. Adsorption energy of the M^{th} attached Ar atom in Au_nAr_m^+ ($n = 3-7, 9$). The energy is calculated as $E_{\text{ads}} = E(\text{Au}_n\text{Ar}_m^+) - E(\text{Au}_n\text{Ar}_{m-1}^+) - E(\text{Ar})$, with E the total energy. Harmonic zero point energy corrections are applied.

	Au_3Ar_m^+	Au_4Ar_m^+	Au_5Ar_m^+	Au_6Ar_m^+ (Iso1)	Au_6Ar_m^+ (Iso2)	Au_7Ar_m^+	Au_9Ar_m^+ (Iso1)	Au_9Ar_m^+ (Iso2)
m	E_{ads} (eV)							
1	-0.41	-0.30	-0.31	-0.25	-0.25	-0.21	-0.18	-0.21
2	-0.38	-0.28	-0.30	-0.22	-0.22	-0.20	-0.17	-0.21
3	-0.35	-0.23	-0.26	-0.14	-0.16	-0.20	-	-
4	-0.11	-0.19	-0.25	-	-	-	-	-
5	-	-	-0.09	-	-	-	-	-

Table S2. Adsorption energy of the m^{th} attached Ar atom in the four isomers of Au_8Ar_m^+ . The energy is calculated as $E_{\text{ads}} = E(\text{Au}_n\text{Ar}_m^+) - E(\text{Au}_n\text{Ar}_{m-1}^+) - E(\text{Ar})$, with E the total energy. Harmonic zero point energy corrections are applied.

	Iso1	Iso2	Iso3	Iso4
m	E_{ads} (eV)			
1	-0.18	-0.20	-0.17	-0.17
2	-0.17	-0.19	-0.18	-0.16
3	-0.15	-0.17	-0.17	-0.13

2. Integrated intensities of the Au_nAr_m^+ signals in the mass spectrum

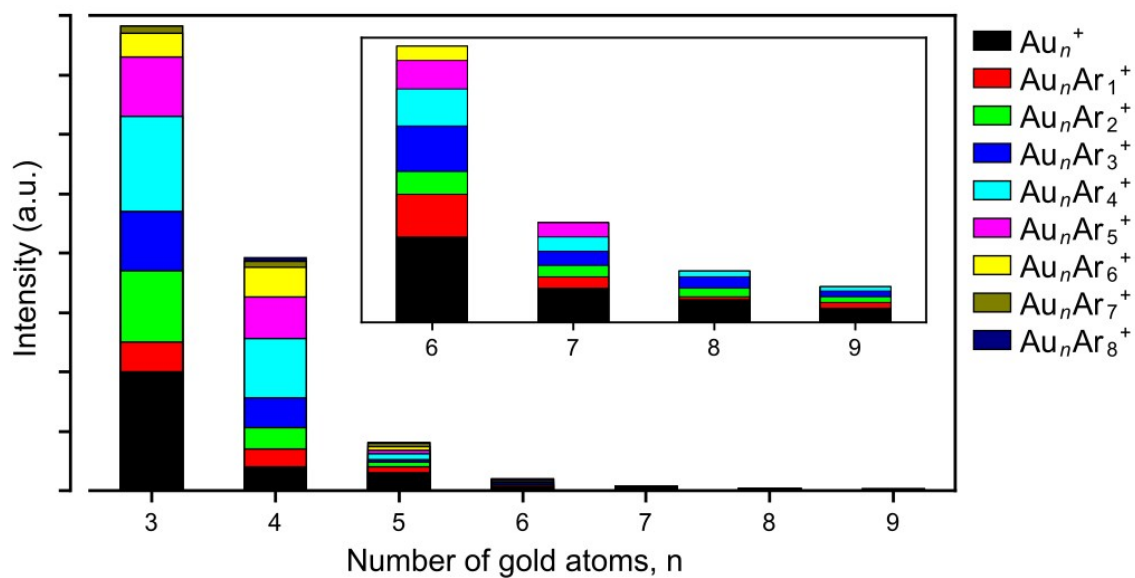


Figure S1. Integrated intensities of Au_nAr_m^+ signals in a representative mass spectrum. The plot shows the intensities (in arbitrary units) of each Au_nAr_m^+ complex in the spectrum. The inset gives a zoom of the $n = 6$ -9 size range.

3. Anharmonic effects in the IR spectrum of Au_8Ar_3^+

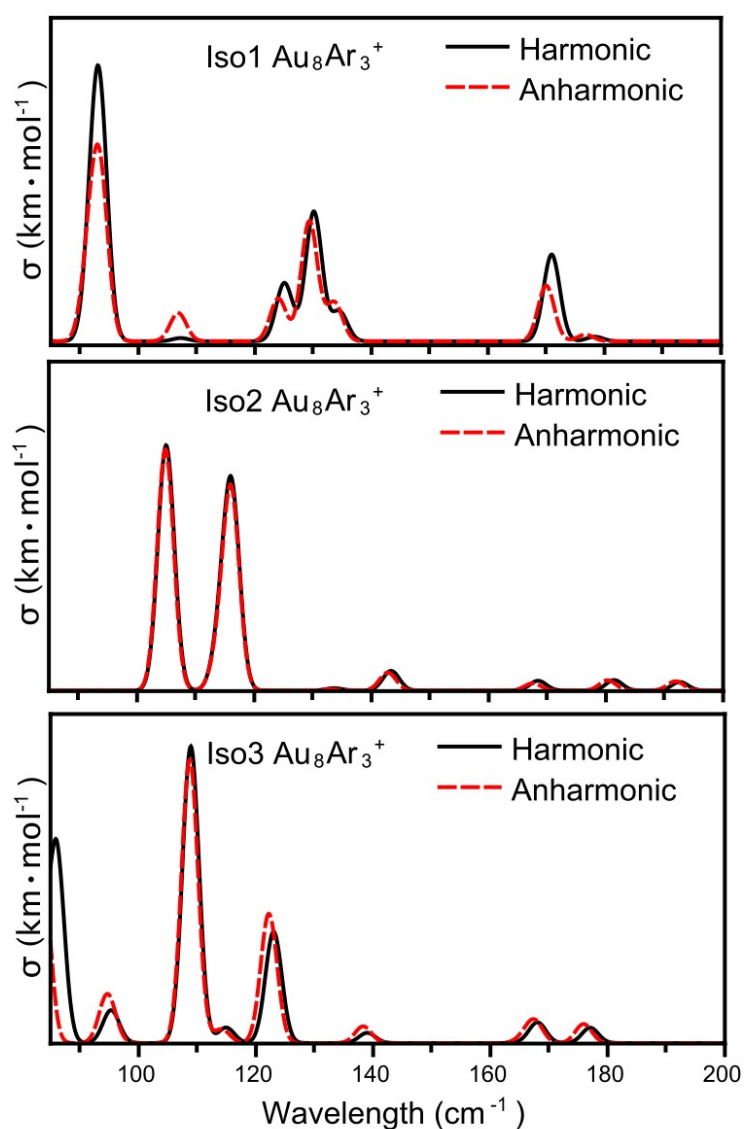


Figure S2. Comparison of the calculated IR spectrum of Iso1, Iso2 and Iso3 of Au_8Ar_3^+ with (dashed red) and without (continuous black) anharmonic effects. Anharmonic calculations are performed with the Gaussian software package [1] at the PBE(D3)/ECP(Def2-TZVP) - GVP2 level.

- [1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A., et al., Gaussian 09, Revision E.01., Gaussian, Inc., Wallingford CT, 2013.

4. The effect of different Ar adsorption configurations

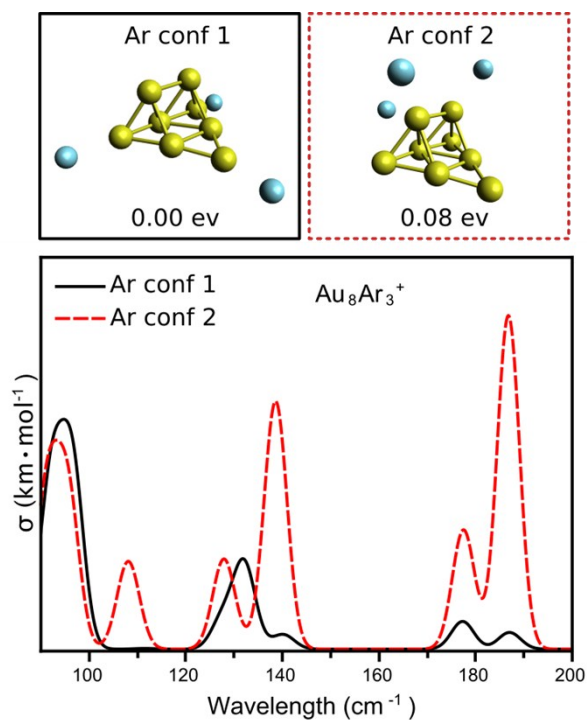


Figure S3. Comparison of the calculated IR spectrum of two Au_8Ar_3^+ complexes in which the metal atom framework is the same (Iso1), but the Ar atoms are at different positions. While the positions of the vibrational modes are similar in both cases, the relative intensities between the bands are different.

5. Cartesian coordinates of the computed structures

Au_3Ar_4^+

Au	0.4272796465	-0.6601416874	-1.3190380606
Au	0.6891699650	1.5086139304	0.1271577102
Au	-0.8086147882	-0.4687270307	0.9903216574
Ar	-2.3765408508	-1.4891620785	2.8153711788
Ar	1.6768031859	3.8978120436	0.5094558060
Ar	0.9567308685	-2.0582353993	-3.4625983150
Ar	2.5975699291	1.7580784467	-2.9627770599

Au_4Ar_3^+

Au	0.3717503239	-1.2521688729	0.7630563358
Au	-0.2347112962	0.8451917061	-0.7789064286
Au	-0.4785617014	1.0264201014	1.8800111878
Au	0.6129465970	-1.4270927167	-1.8862890858
Ar	0.9648815745	-3.3242093889	2.3996274456
Ar	-0.8700991757	3.0140569450	-2.2680872955
Ar	1.2561505056	-2.8705441330	-4.1076722142

Au_4Ar_4^+

Au	0.3496550680	-1.1919502771	0.7671335410
Au	-0.2457948462	0.8864971537	-0.7766791777
Au	-0.4959668772	1.0900487989	1.8791993368
Au	0.5998439426	-1.3958151530	-1.8890539637
Ar	0.9685951063	-3.3084176936	2.3435927324
Ar	-0.8617356686	3.0017096807	-2.3559351257
Ar	1.2544000119	-2.8774206319	-4.1487089835
Ar	-1.1508067369	2.5729361223	4.1378926406

Au_5Ar_3^+

Au	-1.4413627806	-1.6834332368	-1.8151268888
Au	1.1295710846	-1.8375674854	-1.7288244382
Au	1.3452614784	1.3946205469	1.5793880228
Au	-0.1085865649	-0.1219478458	-0.1070566038
Au	-1.2262901414	1.6245771890	1.5465828350
Ar	3.6444219091	-2.5945537982	-2.2624122157
Ar	3.9098324971	1.7397718948	2.1943046269
Ar	-3.9951553705	-2.0837961214	-2.4622014122

Au_5Ar_4^+

Au	-1.4351240792	-1.6685771227	-1.8045078791
Au	1.1352501959	-1.8651972311	-1.7515108582
Au	1.3109755205	1.4087813456	1.5868063945
Au	-0.0590758728	-0.1315472929	-0.1098188850
Au	-1.2594585894	1.5995447902	1.5309333483
Ar	3.6327287701	-2.6622121936	-2.3172130521
Ar	-3.7623486563	2.3843329172	2.0880367071
Ar	3.8761667746	1.8197843603	2.2530657716
Ar	-3.9991629707	-2.0793011261	-2.4740593684

Au_5Ar_5^+

Au	-1.4194789543	-1.6532037900	-1.7848601906
Au	1.1524553384	-1.8342767397	-1.7213837254
Au	1.2758678873	1.4447728853	1.6245024326
Au	-0.0596023668	-0.1076747770	-0.0851047523
Au	-1.2919373170	1.6187718001	1.5457076651
Ar	3.6574165658	-2.6207681816	-2.2809337803
Ar	-3.8177410190	2.3679373038	2.0570782526
Ar	3.9237045966	1.6729034394	2.1149719236
Ar	-3.9807336383	-2.0828534935	-2.4682456467
Ar	1.3846080190	3.8109366099	4.0547420248

Au_6Ar_2^+ (Iso1)

Au	-0.8230753009	-1.8266273448	-1.9423832902
Au	1.7795472541	-1.7060755851	-1.4695678812
Au	1.0103444648	1.5764965941	1.7822535615
Au	0.0254157263	-0.1337980757	-0.0978718300

Au	-1.5873338475	1.4361036939	1.2884229727
Au	2.7509311375	0.0026288926	0.4091015756
Ar	-4.0921542428	2.3685347698	1.8999737944
Ar	-2.8407215629	-2.9827729059	-3.3952087427

Au₆Ar₂⁺ (Iso2)

Au	-1.8911168660	0.0235961071	-2.3668787815
Au	0.1362321894	1.1402815359	-1.1427850141
Au	-1.0493220120	-1.0433166107	-0.1285893460
Au	1.1287220346	0.0760347141	1.2770415401
Au	2.1513132375	2.2021373806	0.1285385568
Au	-0.1602098350	-2.0541661236	2.1054095987
Ar	4.2022906428	3.9551263248	0.6623575907
Ar	0.0204802262	-3.7594272052	4.2559241384

Au₆Ar₃⁺ (Iso1)

Au	-0.9580163418	-1.8213714541	-1.9542010138
Au	1.6667876434	-1.7684096746	-1.5486498908
Au	0.9917341135	1.5458824415	1.7452982435
Au	0.0240593589	-0.1574013319	-0.1225968627
Au	-1.6170114682	1.4159260203	1.2624106651
Au	2.7492597620	-0.0630958027	0.3409388170
Ar	-4.1335391514	2.3510520175	1.8774411295
Ar	-3.0600967038	-2.9178695786	-3.3559017480
Ar	5.6169689101	0.0347024032	0.8301940629

Au₆Ar₃⁺ (Iso2)

Au	-1.7810256047	0.0614273663	-2.2812250475
Au	0.2789355763	1.2820712272	-1.1329534545
Au	-0.9539674400	-1.0396631141	-0.0155167770
Au	1.0838005370	0.0124768190	1.2974825046
Au	2.2984333978	2.1687998632	0.3463986771
Au	-0.1304173038	-2.1444988841	2.2505658704
Ar	4.1480966578	4.2144199471	0.3039471101
Ar	-3.3556460188	0.3376008957	-4.5295460650
Ar	-0.3626213152	-4.1608066603	4.2521842095

Au₇Ar₂⁺

Au	-1.6276098225	-0.2739153251	-2.1193768006
Au	-0.2767802275	2.0338335016	-1.7051658141
Au	-1.2987820328	-2.4026073702	-0.4775712876
Au	0.0635025076	-0.1042467370	-0.0457304002
Au	1.4168520995	2.1778996359	0.3826083377
Au	0.4211192843	-2.1874663414	1.6037379945
Au	1.7909749143	0.1019271317	2.0552478286
Ar	-3.3901076133	-0.4557023769	-4.2760033829
Ar	0.7885802127	-4.3606632955	3.3163048680

Au₇Ar₃⁺

Au	-1.6289314842	-0.2753626045	-2.1013942219
Au	-0.1051572323	1.9416726562	-1.8552527511
Au	-1.4058203917	-2.3592145673	-0.3963552532
Au	0.1525130674	-0.1390346467	-0.1106817443
Au	1.6804465606	2.0385220558	0.1698034398
Au	0.4058916130	-2.1801171707	1.5995910087
Au	1.9685777522	0.0003104835	1.9193899322
Ar	-3.4924125128	-0.4212601786	-4.1804325743
Ar	0.6668775173	-4.3165384871	3.3839083967
Ar	3.2744780030	4.3169181942	0.4601462954

Au₈Ar⁺ (Iso1)

Au	1.9365832561	1.1629422001	-2.2103205517
Au	-0.1406159672	-0.6543723344	-1.8880145728
Au	0.0728587277	1.7293560296	-0.3436834404
Au	1.9603055701	-0.3976354689	0.0309486338
Au	-2.0110596084	-0.2148972178	0.0552496369
Au	-1.7491808125	2.0568555223	1.6185081734
Au	0.0469053623	0.0533852809	2.0302296133

Au	2.0972534152	-1.5655210377	2.3927781063
Ar	3.6793523566	1.9169564317	-4.3262957691

Au₈Ar⁺ (Iso2)

Au	0.5905836273	-2.7749086088	-2.1780723423
Au	-2.3532384242	0.8347978250	-2.4807385955
Au	-0.4644667147	-0.5369365294	-1.2558680738
Au	-1.4466659292	1.7733724632	-0.1516891529
Au	1.5153908757	-1.8706309072	0.1443899531
Au	0.5243137030	0.4559019042	1.2535154722
Au	-0.5307772058	2.6957421114	2.1751864140
Au	2.4115825910	-0.9282928416	2.4665710125
Ar	-4.2020966977	1.4814936258	-4.4360582836

Au₈Ar⁺ (Iso3)

Au	-1.8348616777	0.1661927112	-2.0198360602
Au	0.0845536226	2.1320783341	-1.8579826828
Au	-1.8495927026	-1.8372084661	-0.2193975346
Au	0.0657561056	0.1146148854	-0.0454224039
Au	1.9538457797	2.0565978958	0.1084177105
Au	0.0663174804	-1.9142196166	1.7946206779
Au	1.9409028599	0.0124962814	1.9516518147
Au	-1.8130287943	-3.7888440955	1.5861933295
Ar	-2.8554862711	-6.1769049893	2.6936931789

Au₈Ar⁺ (Iso4)

Au	-4.9804102960	3.4315698923	-0.2114771217
Au	-2.2065880285	3.3292320520	-0.2995234590
Au	-6.3171187576	1.0008541030	-0.1562578539
Au	-3.6498244924	0.8110016455	-0.3021955365
Au	-0.9789610787	0.8276220259	-0.3093685214
Au	-3.4981422638	4.2584144409	2.0346858879
Au	-4.9657337370	1.8571274284	2.1108505595
Au	-2.1917718132	1.7536200584	2.0221152088
Ar	1.7463784706	0.1246492959	-0.8189219870

Au₈Ar₂⁺ (Iso1)

Au	1.9291289627	1.1624069032	-2.2020955875
Au	-0.1335403866	-0.6712060348	-1.8884484626
Au	0.0681917444	1.7139414625	-0.3265798326
Au	1.9689696115	-0.4144945988	0.0255569397
Au	-2.0057532668	-0.2151068275	0.0549449046
Au	-1.7597837677	2.0606336109	1.6282554640
Au	0.0474057289	0.0528480426	2.0202575496
Au	2.0951725094	-1.5686780320	2.3952377198
Ar	3.6719762088	1.9449159118	-4.3291837756
Ar	-3.5331446625	3.6916465432	3.1674527366

Au₈Ar₂⁺ (Iso2)

Au	0.5938947039	-2.7814340035	-2.1790906655
Au	-2.3522546631	0.8346103491	-2.4786171057
Au	-0.4655396949	-0.5401854685	-1.2604257463
Au	-1.4420916617	1.7682779569	-0.1497080829
Au	1.5103895578	-1.8621808607	0.1445882371
Au	0.5338497215	0.4463872991	1.2554306551
Au	-0.5252428711	2.6878631327	2.1749872891
Au	2.4206194040	-0.9276837533	2.4743237417
Ar	-4.2100571090	1.4908701272	-4.4372479565
Ar	4.2911622902	-1.6241668440	4.4064950550

Au₈Ar₂⁺ (Iso3)

Au	-1.8454467505	0.1535806808	-2.0219506247
Au	0.0778506982	2.1204021115	-1.8506527246
Au	-1.8402256134	-1.8331943901	-0.2147916144
Au	0.0704932757	0.1245837979	-0.0509362252
Au	1.9658607961	2.0679244099	0.1128484685
Au	0.0719349076	-1.9136278006	1.7991550545
Au	1.9369675475	0.0113249351	1.9459746379
Au	-1.8154663275	-3.7855199393	1.5810922991
Ar	-2.8635621313	-6.1806708649	2.6911987590
Ar	-0.0790483253	4.1184554517	-3.8235117025

Au₈Ar₂⁺ (Iso4)

Au	-4.9744109956	3.4358499110	-0.2078160923
Au	-2.1955535642	3.3529442681	-0.2811728414
Au	-6.3302793501	1.0048996822	-0.1537049314
Au	-3.6639377851	0.8380596764	-0.2829439794
Au	-0.9892991295	0.8435040518	-0.2958280719
Au	-3.4980898451	4.2783635494	2.0443909462
Au	-4.9614089121	1.8668444801	2.1124441602
Au	-2.1826079989	1.7820217002	2.0377417089
Ar	-9.1152194456	0.3909947163	-0.5442088236
Ar	1.7283982747	0.0756158898	-0.8533215488

Au₈Ar₃⁺ (Iso1)

Au	1.9245046728	1.1621597637	-2.2036652438
Au	-0.1387577031	-0.6630182793	-1.8931593173
Au	0.0572872446	1.7305095696	-0.3405574013
Au	1.9573402504	-0.4066932225	0.0365136329
Au	-2.0096937803	-0.2072621703	0.0484414537
Au	-1.7629240183	2.0608794018	1.6233391720
Au	0.0570531813	0.0566365660	2.0079384319
Au	2.1042065397	-1.5683255240	2.4045208636
Ar	3.6959151513	1.9223209827	-4.3378416707
Ar	-3.5471953115	3.6799028269	3.1934439565
Ar	3.4224703231	-3.3477769129	4.2421319965

Au₈Ar₃⁺ (Iso2)

Au	0.5912387803	-2.7861214168	-2.1826799840
Au	-2.3496868209	0.8354546582	-2.4754448944
Au	-0.4618444367	-0.5465566834	-1.2611627934
Au	-1.4415602835	1.7663681143	-0.1492855593
Au	1.5011704817	-1.8503880657	0.1444991849
Au	0.5335666923	0.4538943216	1.2644118610
Au	-0.5324015957	2.6926843375	2.1744007762
Au	2.4225606753	-0.9262445799	2.4767565856
Ar	-4.2184176674	1.4914483568	-4.4542587729
Ar	4.3101038521	-1.6381811075	4.4134990175
Ar	1.0011580707	-4.9448833810	-3.9344781444

Au₈Ar₃⁺ (Iso3)

Au	-1.8372077380	0.1536103513	-1.9917691959
Au	0.0903844389	2.1271290781	-1.8484701200
Au	-1.8278293552	-1.8308923586	-0.1958029748
Au	0.0902351339	0.1362783258	-0.0344761491
Au	1.9737488645	2.0546695849	0.1255079857
Au	0.0890499587	-1.9054419128	1.8110513242
Au	1.9556151883	0.0055200606	1.9778051194
Au	-1.7826775825	-3.7833132470	1.6092464712
Ar	-2.9414195394	-6.1898054860	2.6050867088
Ar	4.0751330462	3.9175093541	0.5555254047
Ar	-0.1679187762	4.0797837697	-3.8959147728

Au₈Ar₃⁺ (Iso4)

Au	-4.9705788320	3.4198365842	-0.2106361351
Au	-2.2017130204	3.3378059376	-0.2839463812
Au	-6.3282824441	0.9869593482	-0.1659705464
Au	-3.6653560642	0.8102199454	-0.3020430195
Au	-0.9930422051	0.8268638678	-0.3082526873
Au	-3.4989230894	4.2739528727	2.0443822651
Au	-4.9572428821	1.8543010663	2.0998400890
Au	-2.1884396128	1.7704458762	2.0252710371
Ar	-9.1446234587	0.4303731928	-0.5195960263
Ar	1.7614061536	0.1137054438	-0.8287374449
Ar	-3.3792732128	6.7576470268	3.7468402389

Au₉Ar⁺ (Iso1)

Au	1.9399788800	0.8622989100	-2.1064932800
Au	-0.1960386700	-0.7581124100	-1.7627322800
Au	-2.4432660900	-2.0830554900	-1.5088396800
Au	0.1224435600	1.6597045500	-0.2735964000
Au	1.8294842900	-0.5880579700	0.1718287000
Au	-2.1105893600	-0.1026240400	0.1728607800
Au	-1.7302386300	2.1409542000	1.6241177700
Au	-0.0735865200	0.0682952900	2.1181969300
Au	1.7863012100	-1.7291579100	2.5311578400
Ar	3.7001263300	2.2079998300	-4.0631641600

Au₉Ar⁺ (Iso2)

Au	2.1687606200	1.0197630600	-2.2446973400
Au	0.0202941000	-0.6284972500	-2.0107828200
Au	-1.2696028500	-2.5025682100	-0.6396444100
Au	0.3396288600	1.7626977200	-0.4347257700
Au	2.0359509900	-0.5276834900	-0.0153554300
Au	-1.9082594500	0.0216856300	-0.0942960800
Au	-1.5207354700	2.2607319600	1.4181992000
Au	0.1046762400	0.1227359000	1.8994663900
Au	0.7901020200	-2.3980316600	1.3998869800
Ar	-3.3451659800	3.8208340700	3.1744492600

Au₉Ar₂⁺ (Iso1)

Au	2.0282314943	0.8294370982	-2.1661802717
Au	-0.1074061639	-0.7912885819	-1.8280753179
Au	-2.3958596063	-2.0571404250	-1.6163905699
Au	0.2027427458	1.6068359697	-0.3226499870
Au	1.9239797879	-0.6219323473	0.1108362411
Au	-2.0183349789	-0.1225702637	0.1154496767
Au	-1.6547401188	2.1191186114	1.5802809945
Au	0.0131812575	0.0463679945	2.0537435124
Au	1.9250623517	-1.6930409916	2.5063286107
Ar	3.7440892081	2.1684018306	-4.0678136075
Ar	-2.9042437239	4.4823889853	2.6785063249

Au₉Ar₂⁺ (Iso2)

Au	2.0734576600	1.0309004600	-2.1441581400
Au	-0.0810403100	-0.6244273600	-1.9000421700
Au	-1.3715191900	-2.5045347500	-0.5292887300
Au	0.2427615300	1.7524699400	-0.3318672000
Au	1.9300525600	-0.5245978700	0.0907665100
Au	-2.0126634200	0.0189176900	0.0176862300
Au	-1.6183671000	2.2609515500	1.5208684900
Au	-0.0014228100	0.1200553000	2.0092076100
Au	0.6854147400	-2.4000710800	1.5078788400
Ar	-3.4487153600	3.8227236200	3.2833818200
Ar	4.1482805800	1.3427159100	-4.2652182700