

Ultrafast Structural Dynamics in Rydberg Excited *N, N, N', N'*-Tetramethylethylenediamine: Conformation Dependent Electron Lone Pair Interaction and Charge Delocalization

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Supporting Information

Analysis of the binding energy spectrum

To analyze the spectral components of the partially overlapping 3s peaks in the Rydberg electron binding energy spectrum, the spectrum was fitted at each delay time with two Lorentzians, each with variable center binding energy. The results of those fits are shown in Fig. S1. Symbols are the fitted peak centers at different delay time points. Solid lines

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show the best fits of the centers of the two peak components. Only the peak centers after one internal conversion lifetime were included in the fits. The average binding energies are found to be 2.704 (0.004) eV and 2.841(0.004) eV, respectively. Values in the parentheses are the uncertainties (3σ) of the fits. The accuracy of the wavelength measurement and the photoelectron spectrometer, each estimated to be ± 0.005 eV, dominate the overall uncertainty of ± 0.008 eV.

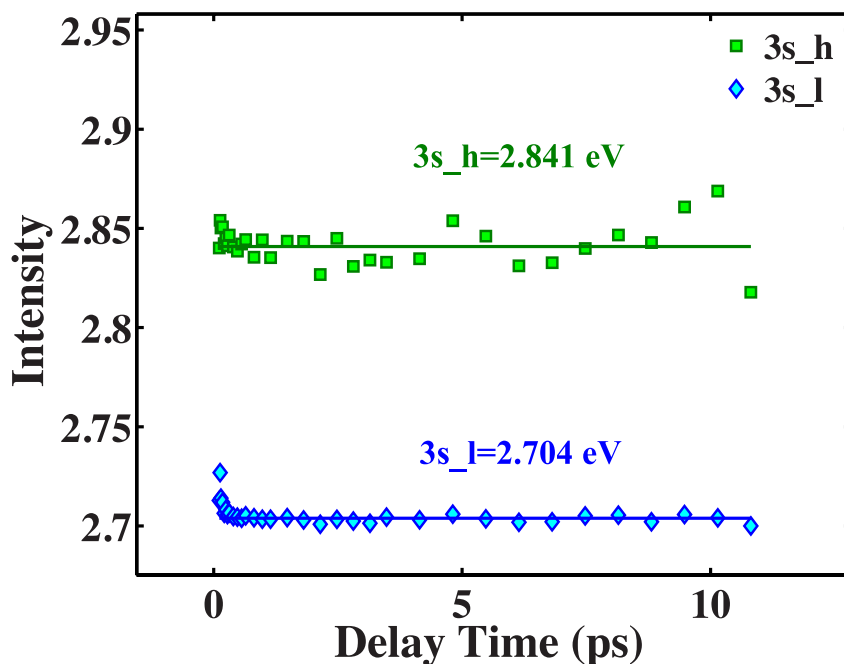


Fig. S1. The peak centers of the deconvoluted 3s peak with higher binding energy (3s_h, green square and line) and lower binding energy (3s_l, blue diamond and line).

Vibrational energy content of TMEDA in the 3p and 3s Rydberg states

The vibrational energy deposited in the 3p and 3s Rydberg excited states can be calculated by the following equation:

$$E_{vib} = h\nu_{pump} + E_b - IP_a$$

ν_{pump} is the wavelength of the pump photon, 209 nm (5.93 eV) in the current work. E_b is the binding energy of specific state, obtained in the photoelectron spectrum. IP_a is the adiabatic ionization potential, which can be estimated by subtracting the minimum energies of the ion state and the ground state surface. A DFT calculation using the PBE1PBE functional and Aug-cc-pVDZ basis set gives 7.67 eV and 6.81 eV for the vertical and adiabatic IP respectively. Because the vertical IP from NIST is given as 7.61 eV with the photoelectron spectroscopy (PE) method², the adiabatic IP is then estimated as $IP_a = 6.75$ eV. Since 3p has a binding energy of $E_b = 2.15$ eV, and 3s₁ a binding energy of $E_b = 2.70$ eV, these states therefore have 1.34 eV and 1.89 eV of energy deposited into the vibrational manifolds, respectively.

Assuming an equipartitioned energy distribution among all the vibrational modes and with the set of vibrational frequencies³ calculated by MP2/Aug-cc-pVDZ using the global minimum ion TTT⁺ structure, the effective vibrational temperatures can be estimated as 756 K and 915 K for the 3p and 3s states, respectively. A detailed description of the vibrational energy and effective vibrational temperature estimation is found in the reference³⁷.

Structures of TMEDA and TMEDA⁺ conformers

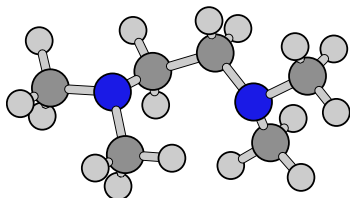
Fig. 4 and Fig. 5 show the conformeric forms of the TMEDA molecule and molecular ion, respectively. Tables S1. and S2. provide the geometrical atom coordinates for the conformers shown in the figures.

² <http://webbook.nist.gov/cgi/cbook.cgi?ID=C110189&Units=SI&Mask=20#ref-3>

³ Vibrational frequencies in cm⁻¹: 41, 83, 139, 146, 172, 174, 182, 204, 206, 362, 410, 439, 464, 479, 501, 781, 809, 840, 850, 1035, 1056, 1059, 1087, 1090, 1105, 1116, 1139, 1154, 1224, 1250, 1260, 1294, 1354, 1362, 1363, 1382, 1425, 1426, 1447, 1459, 1462, 1467, 1472, 1476, 1479, 1480, 1500, 1504, 1506, 1656, 3013, 3013, 3017, 3030, 3075, 3091, 3135, 3135, 3135, 3137, 3154, 3171, 3188, 3189, 3191, 3192

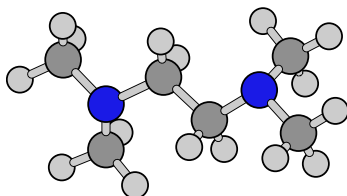
Table S1. Cartesian coordinates of the TMEDA conformers in the ground state.

Conformer GGG'



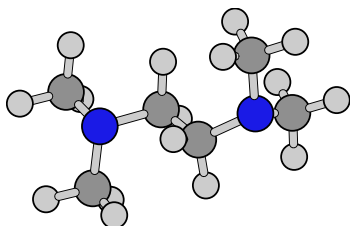
GGG'	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	1.6412680	0.1142343	-0.3929771
C	0.7500597	0.7356251	0.5922188
C	-0.6607416	1.0218754	0.0702938
N	-1.5007385	-0.1520997	-0.1966733
C	3.0336324	0.3129009	0.0145262
C	1.3807726	-1.3250544	-0.5135335
C	-2.7318069	0.2831670	-0.8570073
C	-1.8359824	-0.8506341	1.0439588
H	1.1809148	1.7181555	0.8516121
H	0.7211107	0.1491948	1.5398723
H	-0.5559124	1.5803963	-0.8744295
H	-1.1658183	1.6946491	0.8071681
H	-3.3639892	-0.5916662	-1.0737841
H	-3.3182048	0.9930316	-0.2289562
H	-2.4845271	0.7811644	-1.8066731
H	-2.3432651	-0.1815371	1.7768242
H	-2.5091795	-1.6914206	0.8163816
H	-0.9304371	-1.2585625	1.5148433
H	3.7005506	-0.1568850	-0.7247349
H	3.2620330	1.3888494	0.0572784
H	3.2505842	-0.1352506	1.0116983
H	1.5743673	-1.8570161	0.4474198
H	0.3364136	-1.4851812	-0.8087756
H	2.0460503	-1.7501439	-1.2809330

Conformer GTG



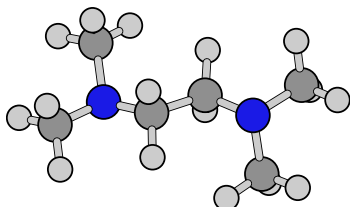
GTG	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.8641112	0.1955692	-0.3531364
C	-0.5918659	-0.4864457	-0.0871314
C	0.5918033	0.4863421	-0.0871331
N	1.8641105	-0.1955831	-0.3531487
C	-2.9277153	-0.8014066	-0.4800816
C	-2.1934290	1.1198090	0.7338600
C	2.1935508	-1.1197449	0.7338524
C	2.9276504	0.8014435	-0.4801273
H	-0.4220627	-1.2189021	-0.8941313
H	-0.6469370	-1.0446401	0.8765980
H	0.6468447	1.0445394	0.8765985
H	0.4219448	1.2187886	-0.8941338
H	3.1771195	-1.5737813	0.5389841
H	2.2331957	-0.6050619	1.7218012
H	1.4505742	-1.9278428	0.7901224
H	3.0596314	1.3989168	0.4509836
H	3.8797005	0.2973199	-0.7067603
H	2.6903293	1.4898774	-1.3053482
H	-3.8797550	-0.2972334	-0.7066314
H	-2.6904757	-1.4898136	-1.3053532
H	-3.0596642	-1.3989431	0.4509922
H	-2.2327589	0.6052335	1.7218706
H	-1.4505417	1.9280099	0.7898431
H	-3.1771059	1.5736462	0.5391258

Conformer GTT



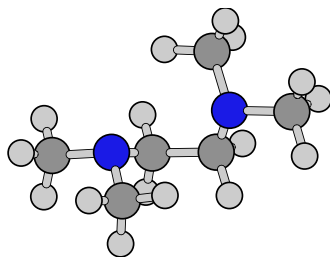
GTT	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	1.7807466	0.2174386	-0.3013765
C	0.4353362	0.2044309	0.2863093
C	-0.5748951	-0.5495653	-0.5990784
N	-1.9936872	-0.2948869	-0.3152603
C	2.6574590	1.0614804	0.5112980
C	2.3341396	-1.1371155	-0.3621687
C	-2.3969672	1.0769102	-0.6153016
C	-2.3624015	-0.6548097	1.0526709
H	0.1162851	1.2549497	0.3885501
H	0.4593288	-0.2362249	1.3107027
H	-0.4207969	-1.6379822	-0.5092251
H	-0.3819909	-0.2695853	-1.6492357
H	-3.4941352	1.1500371	-0.5485527
H	-1.9678184	1.8340545	0.0769028
H	-2.0948529	1.3322858	-1.6426444
H	-1.9214542	0.0160909	1.8218917
H	-3.4583229	-0.6099471	1.1557214
H	-2.0370153	-1.6861469	1.2616645
H	3.6603698	1.0962710	0.0583209
H	2.2542851	2.0851316	0.5469500
H	2.7562699	0.6853643	1.5552689
H	2.3561123	-1.6241418	0.6402500
H	1.7443216	-1.7648636	-1.0446154
H	3.3639713	-1.0911403	-0.7478685

Conformer GTG'



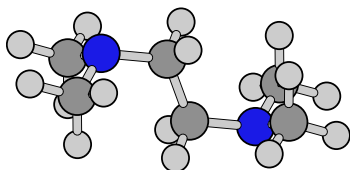
GTG'	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.8509573	-0.0603578	-0.3520238
C	-0.6028411	-0.3638996	0.3575941
C	0.5882899	0.4266129	-0.1900773
N	1.8611415	-0.0621378	0.3560670
C	-2.9079643	-0.9510004	0.1292196
C	-2.2541929	1.3301293	-0.1325707
C	2.9073181	0.9392106	0.1395967
C	2.2623751	-1.3139087	-0.2901584
H	-0.4168443	-1.4424791	0.2361497
H	-0.6953860	-0.1647695	1.4502598
H	0.4952198	1.4843332	0.1031649
H	0.5747612	0.3846677	-1.3036700
H	3.8595138	0.5713301	0.5518603
H	3.0587689	1.1650575	-0.9406595
H	2.6399525	1.8722699	0.6581115
H	2.3977487	-1.1885491	-1.3885569
H	3.2141492	-1.6582907	0.1423890
H	1.5113361	-2.0977163	-0.1205782
H	-3.8409275	-0.7461891	-0.4180946
H	-2.6193752	-1.9976906	-0.0518524
H	-3.1041749	-0.8237266	1.2182738
H	-2.3553840	1.5700594	0.9510473
H	-1.5232420	2.0193721	-0.5783522
H	-3.2253141	1.5069259	-0.6194189

Conformer GG'G



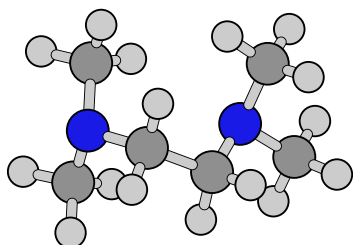
GG'G	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.4523148	-0.0733223	-0.2794349
C	-0.7025810	-0.3053518	0.9549354
C	0.7024633	0.3054796	0.9549218
N	1.4522912	0.0732950	-0.2794360
C	-2.7884999	-0.6504592	-0.1444930
C	-1.5507312	1.3539298	-0.5821967
C	1.5508170	-1.3540180	-0.5820976
C	2.7885190	0.6504280	-0.1444920
H	-0.6409638	-1.3961251	1.1080716
H	-1.2411459	0.1105233	1.8415720
H	1.2409695	-0.1103668	1.8416007
H	0.6408805	1.3962564	1.1079685
H	2.1769361	-1.4884036	-1.4774373
H	2.0106141	-1.9313905	0.2536539
H	0.5516355	-1.7565177	-0.7982055
H	3.3755518	0.1737350	0.6744307
H	3.3422496	0.5257449	-1.0877440
H	2.7058436	1.7271942	0.0722699
H	-3.3423615	-0.5253782	-1.0876112
H	-2.7058950	-1.7273220	0.0718730
H	-3.3753917	-0.1739729	0.6746643
H	-2.0108414	1.9314112	0.2533110
H	-0.5514684	1.7564565	-0.7979136
H	-2.1763706	1.4882961	-1.4778750

Conformer TTT



TTT Element	Cartesian coordinates (Angstroms)		
	x	y	z
N	-1.8714846	0.0000296	0.5102099
C	-0.4067706	0.0002243	0.6570585
C	0.4067689	0.0000765	-0.6570317
N	1.8714851	0.0000224	-0.5102220
C	-2.3736971	1.2022352	-0.1525618
C	-2.3734311	-1.2024457	-0.1522715
C	2.3735281	-1.2023810	0.1523138
C	2.3736036	1.2022991	0.1525051
H	-0.1441283	-0.8873599	1.2574336
H	-0.1443339	0.8880901	1.2571069
H	0.1442469	0.8877575	-1.2573192
H	0.1441804	-0.8876913	-1.2571596
H	3.4710819	-1.2314934	0.0606395
H	2.1243692	-1.2560942	1.2341929
H	1.9627714	-2.0947153	-0.3457933
H	2.1245580	1.2557755	1.2344199
H	3.4711427	1.2314432	0.0606966
H	1.9627644	2.0947296	-0.3453644
H	-3.4712497	1.2312492	-0.0608472
H	-1.9630177	2.0947264	0.3453303
H	-2.1245768	1.2557399	-1.2344596
H	-2.1244125	-1.2560943	-1.2341859
H	-1.9624444	-2.0947243	0.3457499
H	-3.4709655	-1.2317537	-0.0604306

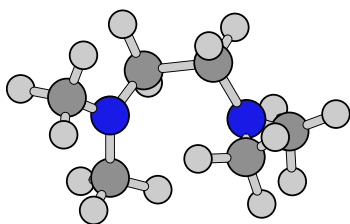
Conformer TGG'



TGG'	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.8184410	0.1247181	0.1979403
C	-0.7834276	-0.0058147	1.2290313
C	0.5462810	-0.6706606	0.8314401
N	1.2553120	-0.0169838	-0.2724937
C	-1.6126845	1.2482609	-0.7193508
C	-2.0296131	-1.1151066	-0.5437820
C	2.3706844	-0.8608515	-0.7031635
C	1.7679003	1.2907172	0.1365836
H	-1.2005905	-0.6213483	2.0486385
H	-0.6067512	0.9961735	1.6542924
H	0.3482871	-1.7116279	0.5253879
H	1.1889072	-0.7265171	1.7456132
H	2.8972062	-0.3788453	-1.5414086
H	3.1047040	-1.0404089	0.1156582
H	1.9862734	-1.8341595	-1.0451486
H	2.4612214	1.2133693	1.0054037
H	2.3125381	1.7479820	-0.7038181
H	0.9417028	1.9613450	0.4101290
H	-2.5202091	1.3687390	-1.3334298
H	-1.4770644	2.1733743	-0.1369111
H	-0.7428672	1.1122416	-1.3917402
H	-1.1832362	-1.3725540	-1.2162124
H	-2.1868246	-1.9467830	0.1623161
H	-2.9362371	-1.0143889	-1.1614482

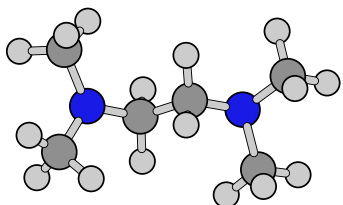
Table S2. Cartesian coordinates of the TMEDA⁺ conformers in the ion ground state.

Conformer GGG⁺



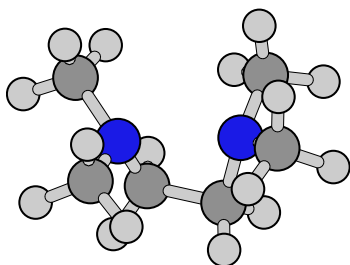
GGG ⁺	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	1.4685039	0.0117719	0.2111840
C	0.6763246	1.1579200	0.4480950
C	-0.6763554	1.1579633	-0.4480155
N	-1.4685358	0.0117991	-0.2112077
C	2.6180022	0.0710059	-0.6837260
C	1.2710924	-1.1260253	1.0917787
C	-1.2710543	-1.1259359	-1.0918640
C	-2.6180011	0.0709156	0.6837482
H	1.2090020	2.0794650	0.1664967
H	0.3519038	1.2054422	1.4994588
H	-0.3519279	1.2055864	-1.4993734
H	-1.2090171	2.0794927	-0.1663356
H	-1.7255508	-2.0257533	-0.6559542
H	-1.7107479	-0.9392654	-2.0887640
H	-0.1836012	-1.2808679	-1.2259811
H	-3.5308702	0.3676716	0.1360255
H	-2.7834963	-0.9159448	1.1396840
H	-2.4261492	0.8091173	1.4766120
H	2.7835321	-0.9158064	-1.1397533
H	2.4261629	0.8092869	-1.4765176
H	3.5308390	0.3677193	-0.1359268
H	1.7109123	-0.9394385	2.0886400
H	0.1836560	-1.2809444	1.2260065
H	1.7255243	-2.0258188	0.6557508

Conformer GTT⁺



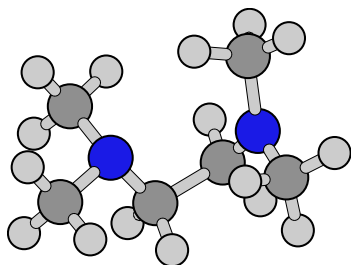
GTT ⁺	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	1.8303262	0.1248841	-0.2879287
C	0.5169067	0.2890118	0.3082976
C	-0.5566714	-0.2190765	-0.7051739
N	-1.8741596	-0.0314047	-0.1393281
C	2.7977287	1.0188677	0.3716126
C	2.2917236	-1.2670234	-0.1903466
C	-2.5157610	1.2687575	-0.1729461
C	-2.5158166	-1.1277923	0.5625218
H	0.3379362	1.3610072	0.4912333
H	0.3994593	-0.2509980	1.2754898
H	-0.4199843	-1.2884749	-0.9135605
H	-0.4708406	0.3712034	-1.6281945
H	-3.5491574	1.1422332	-0.5347292
H	-2.5599362	1.6636623	0.8577222
H	-1.9542542	1.9486865	-0.8228238
H	-3.3085831	-0.7472413	1.2174872
H	-2.9487937	-1.8078817	-0.1938387
H	-1.7561177	-1.6810785	1.1344364
H	3.7765520	0.8983212	-0.1127509
H	2.4773524	2.0638875	0.2509057
H	2.9081948	0.7944607	1.4531356
H	2.3686127	-1.6061239	0.8647556
H	1.6157362	-1.9444380	-0.7332890
H	3.2819975	-1.3480504	-0.6589742

Conformer GG'G⁺



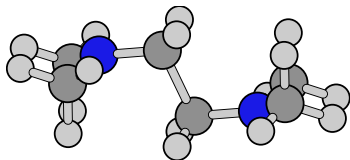
GG'G ⁺	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.1369505	0.0102849	-0.0823543
C	-0.7221877	-0.2539362	1.3131785
C	0.7221642	0.2539208	1.3131808
N	1.1369659	-0.0102758	-0.0823412
C	-1.9219710	-1.0209242	-0.7523117
C	-1.5501818	1.3819901	-0.3701598
C	1.5501666	-1.3819778	-0.3701616
C	1.9219917	1.0209222	-0.7522999
H	-0.7741270	-1.3373033	1.4899163
H	-1.3829636	0.2476794	2.0411106
H	1.3829470	-0.2477081	2.0410994
H	0.7741073	1.3372791	1.4899678
H	1.5111133	-1.5564546	-1.4548286
H	2.5847877	-1.5471800	-0.0149884
H	0.8875495	-2.0933270	0.1408441
H	2.9336527	1.0852044	-0.3066491
H	2.0184521	0.7686761	-1.8177575
H	1.4250652	1.9954022	-0.6454850
H	-2.0186286	-0.7685463	-1.8177202
H	-1.4249025	-1.9953605	-0.6457171
H	-2.9335521	-1.0854076	-0.3065146
H	-2.5848767	1.5471341	-0.0151795
H	-0.8877006	2.0933426	0.1410217
H	-1.5109238	1.5565356	-1.4548097

Conformer TGG⁺



TGG ⁺	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	1.1945693	-0.0255417	-0.2410193
C	0.5895862	-0.5843086	0.9651504
C	-0.7624609	0.1083542	1.2790519
N	-1.5866042	0.0824932	0.0816789
C	1.8087105	1.2835406	0.0408274
C	2.2270595	-0.9451795	-0.7539891
C	-2.0063209	-1.1942596	-0.4626869
C	-1.6884093	1.2606255	-0.7548168
H	1.2235134	-0.4808645	1.8724199
H	0.4123575	-1.6600266	0.8083134
H	-0.6310039	1.1528684	1.5870747
H	-1.2885039	-0.4483224	2.0721195
H	-3.0048425	-1.0853145	-0.9085945
H	-1.2864034	-1.4653528	-1.2578008
H	-2.0069023	-1.9579850	0.3235767
H	-0.7465224	1.3024544	-1.3368244
H	-2.5467974	1.1660432	-1.4311802
H	-1.7720940	2.1551204	-0.1243457
H	2.2396752	1.6870635	-0.8864372
H	1.0571659	2.0015487	0.4041372
H	2.6118937	1.2071945	0.8019074
H	1.7705780	-1.9156009	-0.9996686
H	2.6609531	-0.5210399	-1.6704018
H	3.0421872	-1.1090829	-0.0201345

Conformer TTT⁺



TTT ⁺	Cartesian coordinates (Angstroms)		
Element	x	y	z
N	-1.8239146	0.0000000	0.3714899
C	-0.4489304	0.0000007	0.6823317
C	0.4489020	-0.0000021	-0.6823002
N	1.8238955	-0.0000002	-0.3714558
C	-2.4154014	1.2377501	-0.1231381
C	-2.4154004	-1.2377505	-0.1231388
C	2.4154206	-1.2377566	0.1231154
C	2.4154186	1.2377584	0.1231131
H	-0.1783458	-0.9081190	1.2429103
H	-0.1783461	0.9081225	1.2429069
H	0.1783166	0.9081169	-1.2428784
H	0.1783182	-0.9081242	-1.2428741
H	3.4995138	-1.2165031	-0.0577209
H	2.2478997	-1.3490151	1.2131781
H	1.9742873	-2.0949180	-0.4040464
H	2.2479141	1.3490090	1.2131790
H	3.4995090	1.2165148	-0.0577409
H	1.9742699	2.0949191	-0.4040367
H	-3.4995013	1.2165119	0.0576579
H	-1.9742856	2.0949155	0.4040328
H	-2.2478434	1.3490086	-1.2131971
H	-2.2478608	-1.3489975	-1.2132018
H	-1.9742686	-2.0949171	0.4040165
H	-3.4994974	-1.2165227	0.0576770