Supplementary information

I. Procedure to simulate depletion spectra.

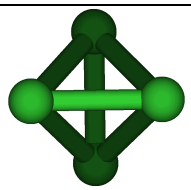
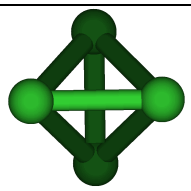
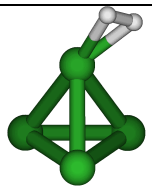
Single photon cross-sections were calculated using DFT. The simulated depletion spectra shown in Figure 1 assume that absorption of the first photon is rate determining in the IR-MPD process. The calculated photon absorption cross sections were convoluted with Gaussians with a width of 20 cm^{-1} and converted into depletion spectra according to:

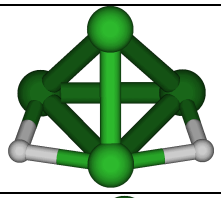
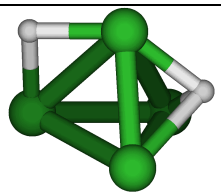
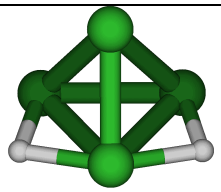
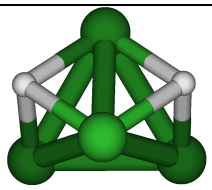
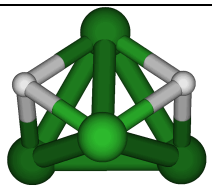
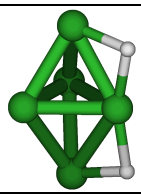
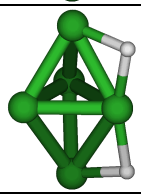
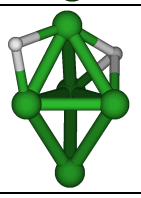
$$\frac{I(\nu)}{I_0} = 10^{-\left(\frac{\sigma(\nu)*P_{FEL}(\nu)}{c}\right)}$$

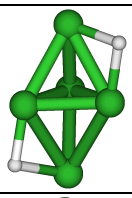
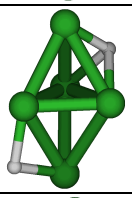
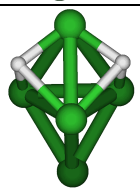
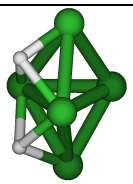
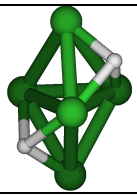
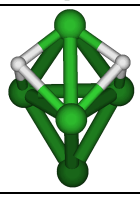
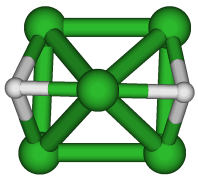
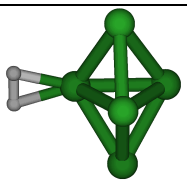
With $\sigma(\nu)$ the calculated single photon cross-section at photon frequency ν, $P_{FEL}(\nu)$ the output power of the free electron laser at frequency ν. The constant c is introduced to obtain the best possible agreement with experiment.

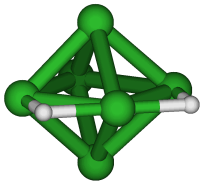
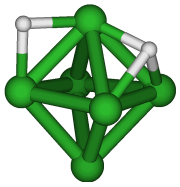
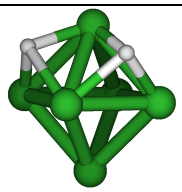
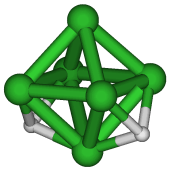
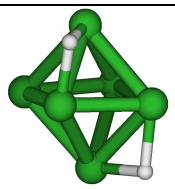
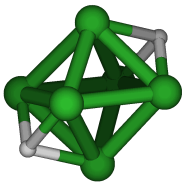
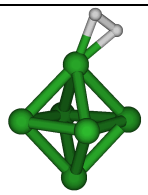
II. Structures and (relative) energies of calculated $Ni_nH_2^+$ clusters

Structures and energies calculated at the BP86/TZVPP level as implemented in the TURBOMOLE package. Transition states and saddle points are indicated by TS and SP. Reported energies include zero point vibrational energy (ZPVE). The letter 'u' denotes the number of unpaired electrons. Coordinates are given in atomic units.

Species	Structure	Energy (H) (incl ZPVE)	ΔE (eV)	Coordinates			
H_2		-1.1679839	0.00	0.00000000000000 0.00000000000000	0.00000000000000 0.00000000000000	-0.70827415135408 0.70827415135408	h h
			Ni_4^+				
Ni_4^+ iso1, u3		-6034.2217098	0.00	0.65335362111132 -1.72845288356709 2.18679400374149 -1.11169474128572	0.52238691656282 -2.01942471621117 -0.65712966622430 2.15416746587264	2.52386435915022 -0.06844109859616 -1.36333776055347 -1.09208550000058	ni ni ni ni
Ni_4^+ iso1, u1		-6034.2050832	+0.45	-1.79944175183514 1.98696074986466 -1.14513619994830 0.95761720191878	0.86841374636601 -1.20636776516861 -1.72917792798675 2.06713194678934	-1.75363647176488 -1.29129625499422 1.66719105741597 1.37774166934312	ni ni ni ni
			$Ni_4H_2^+$				
$Ni_4H_2^+$ molecular, u3		-6035.4079101	0.00	-1.41474524429273 -0.71230710226847 2.61417469397318 -0.67131261606741 5.10431544351350 5.62399062984236	0.90286566871578 1.41355431181575 0.25512793471822 -2.55241376233724 -1.27810960586099 0.16362592331692	-2.07781295677303 2.14301825884840 -0.48624242321024 0.39765496715661 0.73037148728360 0.63154033555213	ni ni ni ni h h

Species	Structure	Energy (H) (incl ZPVE)	ΔE (eV)	Coordinates
$Ni_4H_2^+$ iso2, u3		-6035.4038651	+0.11	2.66335191681687 0.00061861171754 0.14105673894434 ni -1.04138755139197 -0.00027257288070 2.42108858670665 ni -0.84405803569964 -2.29037219874928 -1.27787549706169 ni -0.84505100021428 2.29000807992238 -1.27774712905501 ni 1.95544915717290 -2.95236951199362 -0.18815341179043 h 1.95544462380311 2.95342259513698 -0.19176631762434 h
$Ni_4H_2^+$ iso3, u3		-6035.4039152	+0.11	0.83858305902061 -0.49295671571192 -2.50339829179082 ni -2.45703589392076 0.99787200096936 -0.08202052931242 ni 0.02101554836473 -2.35322915574413 1.44064989951492 ni 1.58119543513771 1.86299708281245 1.19570810185530 ni 0.71500574030655 -3.33638032038050 -1.36910908247481 h 0.23101358126021 2.48114514905053 -1.59788326201366 h
$Ni_4H_2^+$ iso2, u1		-6035.3946984	+0.36	2.64720211814494 0.17940360024213 0.41350400518950 ni -1.31092794292885 -0.00679969190084 2.29906912229134 ni -0.57115689126375 -2.36423788999292 -1.29069657578962 ni -0.83332663733704 2.18728503497979 -1.42083469779389 ni 2.18471824853261 -2.82557220974532 -0.00900965085501 h 1.78818881935215 3.07888000571554 -0.05167394321235 h
$Ni_4H_2^+$ iso1, u3		-6035.3942569	+0.37	-0.48972511011276 2.21013189297980 -1.52465907963310 ni -2.17366797428010 -0.47946555455145 1.56198414268078 ni 0.47583869324173 -2.21158959797387 -1.52681059748513 ni 2.18775238590164 0.48094705208181 1.54291021573002 ni 2.31632167263181 0.50504884799775 -1.56499808300912 h -2.32785403153333 -0.50643466285888 -1.54676421020132 h
$Ni_4H_2^+$ iso1, u1		-6035.3924965	+0.42	-1.14327389582919 2.38754730514239 0.65824536292830 ni -0.47385127399703 -1.79203267865902 1.98046810060230 ni -1.10033633271476 -0.91963129815418 -2.31701654700320 ni 2.75179650306595 0.30034110617848 -0.29512174182495 ni 0.73863040685526 1.79557782493898 -1.99600422218912 h -2.73849933234074 -0.41075144116306 0.44811241312692 h
			$Ni_5H_2^+$	
$Ni_5H_2^+$ iso5, u5		-7544.0591404	0.00	0.00302019152704 -0.00000099216939 -2.51273210758819 ni -2.14483370535721 -0.00019855764073 1.36039347685260 ni 2.14178620673575 0.00019918037144 1.36592973655857 ni -0.00011841351640 3.70262858136344 -0.05429650798718 ni 0.00010534466442 -3.70262818432738 -0.05429529332046 ni 0.00140414612470 -3.05903650674684 -3.05788317547597 h 0.00094758241196 3.05903489931610 -3.05788333354252 h
$Ni_5H_2^+$ iso5, u3		-7544.0560336	+0.08	0.95410263096764 0.00001455657076 -2.39651712695070 ni -2.50130945981779 0.00018442686497 0.24123466695076 ni 1.40241306632358 -0.00019278062298 2.12415969303489 ni 0.05467183301209 3.72325315879381 0.06170218319450 ni 0.05444832545426 -3.72325898316801 0.06158371046847 ni 1.04000518323169 -3.04669804636847 -2.68365642972580 h 1.03783175077962 3.04667600391947 -2.68445687566469 h
$Ni_5H_2^+$ iso7, u5		-7544.0559555	+0.09	-2.15503651158837 -0.09769123079596 -1.32105953829684 ni 0.00034306577408 0.05657464699164 2.50743863884734 ni 2.15791948731457 -0.10132160191189 -1.31919739600067 ni -0.00050246987836 3.74573422154984 -0.00071083923667 ni -0.00273504962099 -3.69135642756722 0.12813250737878 ni -0.00701533466998 3.14737651285592 3.01690593797095 h 0.00768387969146 1.98176978979101 -2.70257516497510 h

Species	Structure	Energy (H) (incl ZPVE)	ΔE (eV)	Coordinates
$Ni_5H_2^+$ iso6, u3		-7544.0553425	+0.10	1.03527667466450 -0.16153919484436 -2.25635712788166 ni -2.47513254300211 0.16750951992280 0.19952787796992 ni 1.42958419319216 -0.00588438234313 2.04139133898991 ni 0.12537808581801 3.78490940210135 -0.04594374950864 ni -0.09042758363973 -3.78515942590399 0.09718890298014 ni 1.33418833902215 -3.20769887636654 -2.45738983537810 h -2.77162589678379 3.21725590630139 0.37176902316042 h
$Ni_5H_2^+$ iso7, u3		-7544.0530872	+0.16	-2.14642223901080 -0.08930200325066 -1.27968847730787 ni 0.00083741752010 0.18623901268174 2.44562455969032 ni 2.14565400034689 -0.09216127675394 -1.28104498307804 ni 0.00073148494260 3.79788962949684 -0.07043743638220 ni -0.00080042932623 -3.81802318669712 0.17762733951425 ni 0.00079354191813 3.22701776941514 2.89534122806994 h -0.00080719895559 -2.33248928369298 -2.43409302925904 h
$Ni_5H_2^+$ iso3, u5		-7544.0523079	+0.19	-2.23300964451780 -0.10850640201605 -1.24108642092385 ni -0.00389229884030 0.03814377406672 2.48071616995511 ni 2.23624781301533 -0.10917002441058 -1.23492685270524 ni 0.00052740318423 3.78355974057698 -0.07663133020954 ni 0.00008262164390 -3.68092482804098 0.03973542719625 ni 2.47671790793653 2.24176379148824 0.93632982796879 h -2.47414894778485 2.23720513125923 0.93877699327547 h
$Ni_5H_2^+$ iso1, u5		-7544.0518017	+0.20	0.00017617813931 -0.00001106546429 -2.53344305968958 ni -2.11591363826305 -0.00000181637574 1.35224698044850 ni 2.11593348005077 -0.00000590970184 1.35241467456498 ni -0.00010425104358 3.73880296596717 -0.13009458307869 ni -0.00010616601292 -3.73878255788772 -0.13009163863746 ni 0.00040045156457 -2.32923776397263 2.59099111010474 h 0.00043812048784 2.32914360747894 2.59099778389901 h
$Ni_5H_2^+$ iso2, u3		-7544.0489576	+0.28	-0.42549567530164 -0.07120724347576 -2.47867490811382 ni -2.06172352260801 0.00484701743477 1.53557610055844 ni 2.42216373321685 0.05895988744007 0.85079171274072 ni 0.01563617384539 3.72450391224698 -0.01542717843512 ni 0.08689115958796 -3.71314010244606 0.07778820840781 ni 0.27696624941345 1.94835914392482 2.50407719622324 h -2.45954451439956 -2.17921461993293 -0.75984525789913 h
$Ni_5H_2^+$ molecular iso1, u3		-7544.0460296	+0.36	-1.24443255523962 0.08108569452949 -2.18915653963400 ni -1.24443332160003 0.08108577951271 2.18915614609046 ni 2.50993071716557 0.00656122057680 0.00000047424145 ni 0.02558693673179 3.67890533507060 -0.00000005980083 ni -0.07673708900142 -3.62630809229923 -0.00000002471999 ni 0.13960160259346 -6.71708092109485 0.00000035193861 h 1.61274089194058 -6.17445416843055 -0.00000012927046 h
$Ni_5H_2^+$ iso3, u3		-7544.0457817	+0.36	-2.22429075929284 -0.11496313675945 -1.37337249837464 ni -0.00297444838071 -0.02604251761921 2.61704661845286 ni 2.22751693525131 -0.11513117157576 -1.36795586497666 ni 0.00000397207859 3.75892048450034 -0.00183082771401 ni -0.00020808367738 -3.56819157991201 0.08780700108166 ni 2.22361609893194 1.90488106786611 1.11845855903483 h -2.22638952882106 1.90485440382866 1.11267937619434 h
$Ni_5H_2^+$ iso8, u3		-7544.0447162	+0.39	-0.00005005600472 -0.00042714080722 -2.56928842540976 ni -3.02195282819932 0.28991524132609 0.71366848057195 ni 3.02181197415387 -0.28986379926058 0.71367308053686 ni 0.30101658764923 3.15915645705579 0.59924040665248 ni -0.30083902050093 -3.15878193870028 0.59966850150367 ni 1.90348819288575 -2.28344953553373 -1.65886063312474 h -1.90271102514352 2.28351828805003 -1.65893810566524 h
$Ni_5H_2^+$ molecular iso2, u5		-7544.0444606	+0.40	-1.79437649399763 -0.00017016232955 -1.80739979895405 ni -0.56535976988411 -0.00004139168605 2.46244376630687 ni 2.40749856100052 0.00032168044797 -0.79818740327058 ni -0.03054604807438 3.63130192006259 -0.01981953755669 ni -0.03024909410713 -3.63130996023421 -0.01997852429837 ni 0.37904887920436 -0.78988785089574 5.32713612633727 h 0.38005936174842 0.78394175689629 5.32843431151561 h

Species	Structure	Energy (H) (incl ZPVE)	ΔE (eV)	Coordinates			
$Ni_6H_2^+$							
$Ni_6H_2^+$ iso5, u5		-9052.7138774	0.00	-0.00004042592260	-0.00000203255443	-3.31786633283772	ni
				-3.20557815002482	-0.00000070755073	-0.21247221221473	ni
				0.00004593472592	0.00000362986485	3.42350231477600	ni
				3.20556987643734	-0.00000078662043	-0.21256390071697	ni
				0.00000193618867	-2.90818023333423	0.21674632153236	ni
				0.00000220037702	2.90818023364520	0.21673950217352	ni
				-3.11205493041131	0.00000180767056	-3.32246131181689	h
				3.11197502992478	-0.00000783320966	-3.32254897534353	h
$Ni_6H_2^+$ iso8, u5		-9052.7114853	+0.07	-0.22600080173344	0.95284851201107	-3.18810607301292	ni
				-0.11894241868632	3.00937169034786	1.03762375059197	ni
				0.16175573996125	-3.10497190268566	-0.85782851222811	ni
				2.95008713544963	0.20533108433899	-0.34085524693674	ni
				0.23505563455941	-0.85310256049497	3.19676592815997	ni
				-2.97459373787062	-0.19591017162711	0.05383808289263	ni
				0.08863533683358	2.12920967840462	4.00449497192288	h
				-1.68233028720722	-2.91940991499118	1.73632981552519	h
$Ni_6H_2^+$ iso1, u5		-9052.7095619	+0.12	-0.01360083841520	0.36585661660495	-3.22105765340539	ni
				-3.25966870534254	-0.03798281874762	0.00200821096038	ni
				0.01419841738148	-0.37800355349158	3.26331902433886	ni
				3.25985803268894	-0.03008258495358	-0.02499378761390	ni
				0.00216101677980	-2.96341274205357	-0.43568557165270	ni
				-0.00325805582281	2.99031601530820	0.32947431715621	ni
				2.39731264509388	1.55570502352737	2.52094725124482	h
				-2.37924872196426	1.54932324430953	2.54267653648037	h
$Ni_6H_2^+$ iso2, u5		-9052.7078100	+0.17	-2.29063874256283	-0.03398574048507	2.22432264883110	ni
				2.23981825421247	-0.03278286170453	2.27610014360963	ni
				2.29085111018919	-0.03246202345043	-2.22467737924495	ni
				-2.23968376992985	-0.03360694396218	-2.27579887780291	ni
				0.00067551369807	-3.11042758278390	-0.00021807866067	ni
				-0.00100613230738	3.16941433455738	0.00026564702085	ni
				0.03386452543657	2.15094782443155	-3.04954592652784	h
				-0.03481004665594	2.15055074668079	3.04988935803721	h
$Ni_6H_2^+$ iso6, u5		-9052.7059223	+0.22	-2.97142890079634	-1.16707793174246	-0.76202990834589	ni
				-1.50509955013699	2.68477795502067	0.85638012734247	ni
				2.94981584153205	1.19407252156572	0.76827045786005	ni
				1.37289946789388	-2.78214764099795	-0.86389731099784	ni
				-0.27699480658941	-1.16995598581774	2.76571770527054	ni
				0.45167972956545	1.16196326431263	-2.72232606505837	ni
				-4.07775386097432	1.70307544594922	-0.50905224145074	h
				2.86206064587486	2.86151930862485	-1.94396918421351	h
$Ni_6H_2^+$ iso3, u3		-9052.7012163	+0.34	-0.66567686712736	2.98095370059603	0.09856892992064	ni
				-0.99598328792049	-0.31628334825720	2.99603847558294	ni
				0.53967406011915	-3.00792999906393	-0.14601380371488	ni
				1.08840736797375	0.31549899150524	-2.96938420262436	ni
				-3.04631530714472	-0.49383462907975	-1.05493053589684	ni
				3.07969786495075	0.52246046129197	1.07193891983493	ni
				3.24356526804219	-1.50157360728408	-1.28041847663043	h
				-3.23213924273111	1.45118069755356	1.50071665421149	h
$Ni_6H_2^+$ molecular, u3		-9052.6940534	+0.54	-3.15986484508265	0.00602871471402	-0.29708230225241	ni
				-0.00829114112491	-3.01314540830616	-0.11905497674997	ni
				3.12703659222959	-0.00541928221923	0.34725776984240	ni
				0.00549270401726	3.01310738478374	-0.12999741429528	ni
				0.34287698949016	-0.00619930272149	-3.25237916704991	ni
				-0.34530019409207	0.00640760307135	3.25068313945798	ni
				0.43052556511280	-0.00834596790269	6.25097729606693	h
				1.78572026538927	-0.03706881062086	5.43155091011067	h

III. Comparison of Experimental and Calculated Spectra of $Ni_nH_2^+$ Complexes

Spectra of all isomers depicted above are shown, together with the experimental spectrum in the low frequency range.

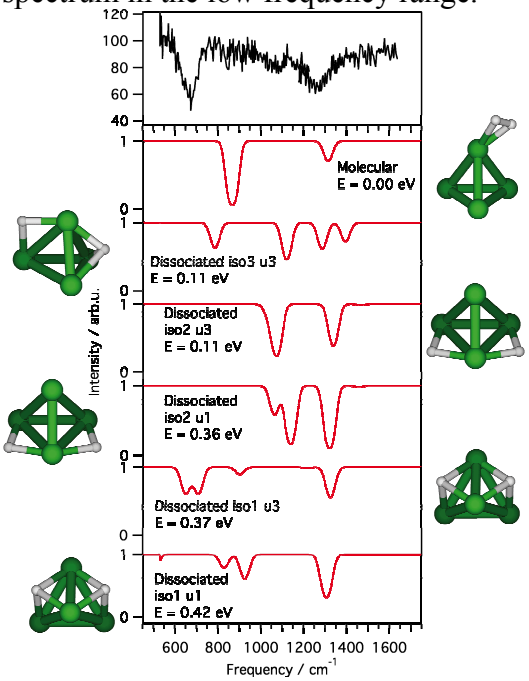


Figure S1. Experimental (black) and calculated (red) vibrational spectra of $Ni_4H_2^+$ complexes in the 450-1750 cm^{-1} range. Relative energies are given in eV. The letter 'u' denotes the number of unpaired electrons. The corresponding cluster structures are shown next to the spectra.

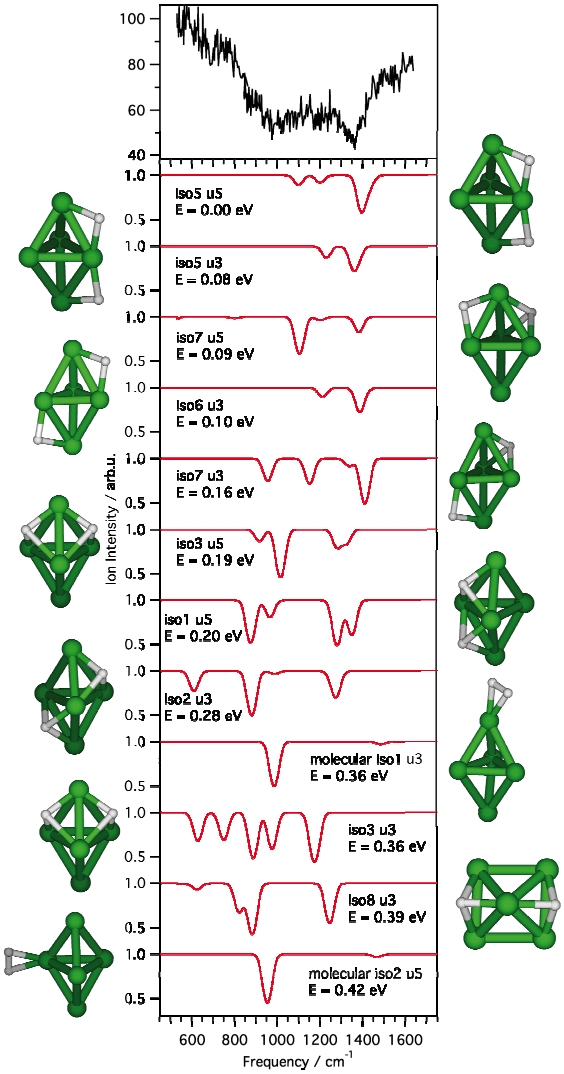


Figure S2. Experimental (black) and calculated (red) vibrational spectra of $Ni_5H_2^+$ complexes in the 450-1750 cm^{-1} range. Relative energies are given in eV. The letter 'u' denotes the number of unpaired electrons. The corresponding cluster structures are shown next to the spectra.

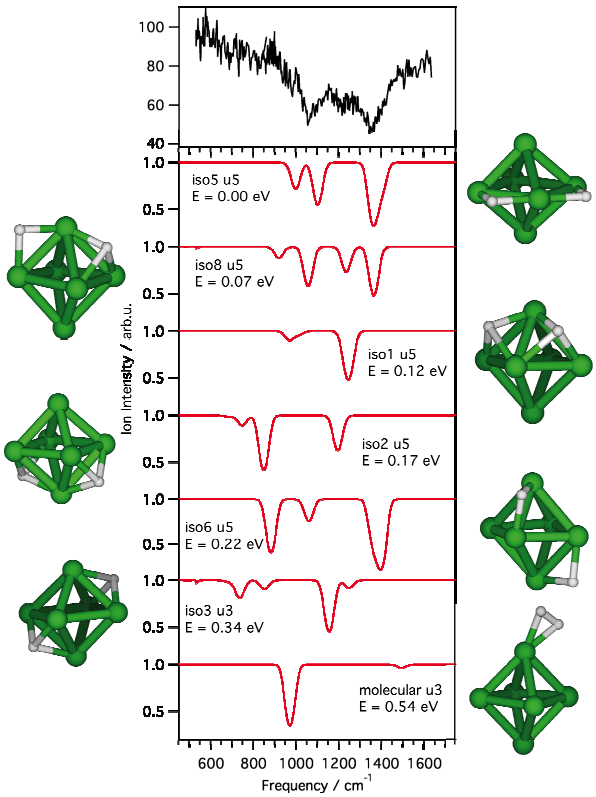


Figure S3. Experimental (black) and calculated (red) vibrational spectra of $Ni_6H_2^+$ complexes in the 450-1750 cm^{-1} range. Relative energies are given in eV. The letter 'u' denotes the number of unpaired electrons. The corresponding cluster structures are shown next to the spectra.