Electronic supplementary information (ESI)

Structural Determination of Niobium-Doped Silicon Clusters by Far-infrared Spectroscopy and Theory

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Table S1. Comparison of the calculated relative energies without (ΔE_1, eV) and with (ΔE_2, eV) inclusion of zero-point vibrational energy (ZPVE) for Si_nNb^+ (n = 7, 9, 10, 11, and 12), using the BP86 and B3LYP functionals in conjunction with def-SVP basis sets.

Cluster		BP86		B3LYP		Cluster		BP86		B3LYP	
		ΔE_1	ΔE_2	ΔE_1	ΔE_2			ΔE_1	ΔE_2	ΔE_1	ΔE_2
Si_7Nb^+	iso1	0.000	0.000	0.18	0.18	Si_9Nb^+	iso1	0.00	0.00	0.00	0.00
	iso2	0.004	0.001	0.000	0.000		iso2	0.09	0.07	0.14	0.13
	iso3	0.30	0.30	0.35	0.34		iso3	0.09	0.07	0.20	0.18
	iso4	0.32	0.31	0.27	0.27		iso4	0.15	0.15	0.08	0.08
	iso5	0.37	0.36	0.36	0.35		iso5	0.21	0.19	0.29	0.27
$Si_{10}Nb^+$	iso1	0.000	0.000	0.000	0.000	$Si_{11}Nb^+$	iso1	0.000	0.000	0.000	0.000
	iso2	0.10	0.10	0.06	0.06		iso2	0.005	0.005	0.044	0.045
	iso3	0.12	0.11	0.17	0.19		iso3	0.15	0.13	0.19	0.17
	iso4	0.16	0.15	0.16	0.15		iso4	0.32	0.33	0.19	0.21
	iso5	0.21	0.21	0.23	0.23		iso5	0.36	0.37	0.10	0.12
$Si_{12}Nb^+$	iso1	0.000	0.000	0.028	0.021						
	iso2	0.12	0.11	0.14	0.11						
	iso3	0.15	0.16	0.21	0.21						
	iso4	0.16	0.17	0.000	0.000						
	iso5	0.26	0.26	0.10	0.10						

Table S2. Average Si−Si and Nb−Si bond distances (R_{Si-Si}, R_{Nb-Si}, Å) and coordination numbers (CNs) of Nb and Si atoms in Si_nNb^+, as well as a comparison of those variables with Si_nV^+.

n	Si_nNb^+				Si_nV^+			
	R_{Si-Si}	R_{Nb-Si}	CN of Nb	CN of Si	R_{Si-Si}	R_{V-Si}	CN of V	CN of Si
4	2.5	2.4	3.1	3.7	2.5	2.3	3.1	3.7
5	2.5	2.5	4.1	4.0	2.5	2.4	4.1	4.0
6	2.6	2.6	5.0	4.3	2.5	2.5	4.0	4.6
7	2.5	2.7	5.9	4.5	2.5	2.6	5.8	4.5
8	2.5	2.7	7.0	4.6	2.5	2.6	6.9	4.6
9	2.5	2.7	7.9	4.8	2.5	2.6	7.8	4.8
10	2.5	2.7	9.0	4.4	2.5	2.6	7.8	4.9
11	2.6	2.8	9.8	4.8	--	--	--	--
12	2.5	2.8	9.9	4.7	2.38	2.7	11.6	4.1

The average bond distances are defined as [1]:

$$\langle R \rangle = \frac{1}{n_b} \sum_{ij} R_{ij} \qquad (1)$$

where R_{ij} is the distance between atoms i and j with a given distance cutoff (3.2 Å), and n_b is the total number of bonds with distances below this cutoff.

The coordination numbers for all atoms are evaluated by the following formula[2]:

$$\mathrm{CN}_A = \sum_{B \neq A} \frac{1}{1 + \exp(-16 * ((4/3)(R_A + R_B)/r_{AB} - 1))} \qquad (2)$$

where R_A and R_B are scaled covalent radii of A and B atoms, respectively, with values as proposed by Pyykkö and Atsumi,[3] and r_{AB} is the internuclear distance between A and B.

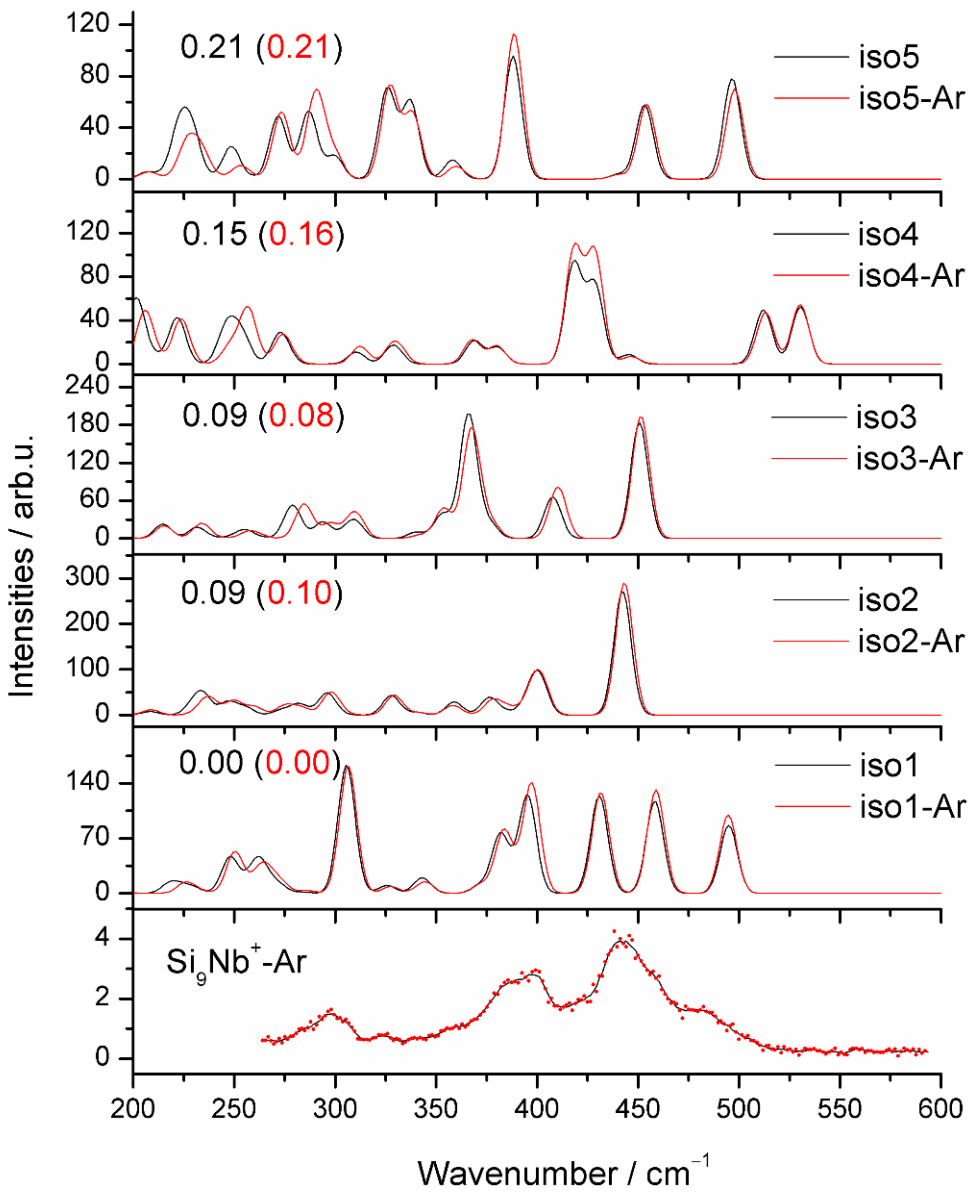
(1) Rao, B. K.; Jena, P. *J. Chem. Phys.* **1999**, *111*, 1890.

(2) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

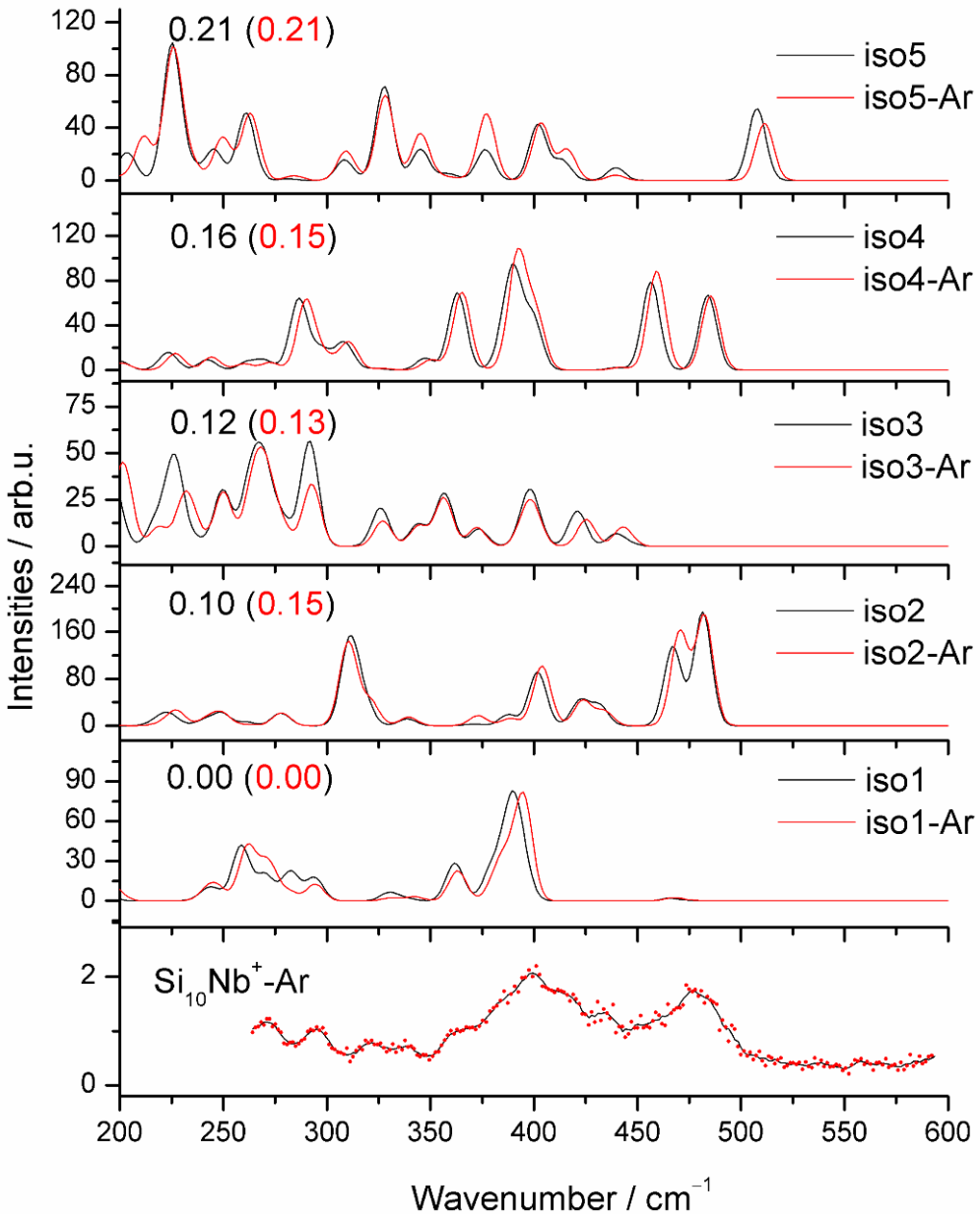
(3) Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, 15, 186.

Table S3. The natural charge population (NCP) and natural electron configuration (NEC) of the Nb dopant in Si_nNb^+ (n = 4−12), obtained at the BP86/def-SVP level of theory using the NBO 3.1 program as implemented in the Gaussian software package.

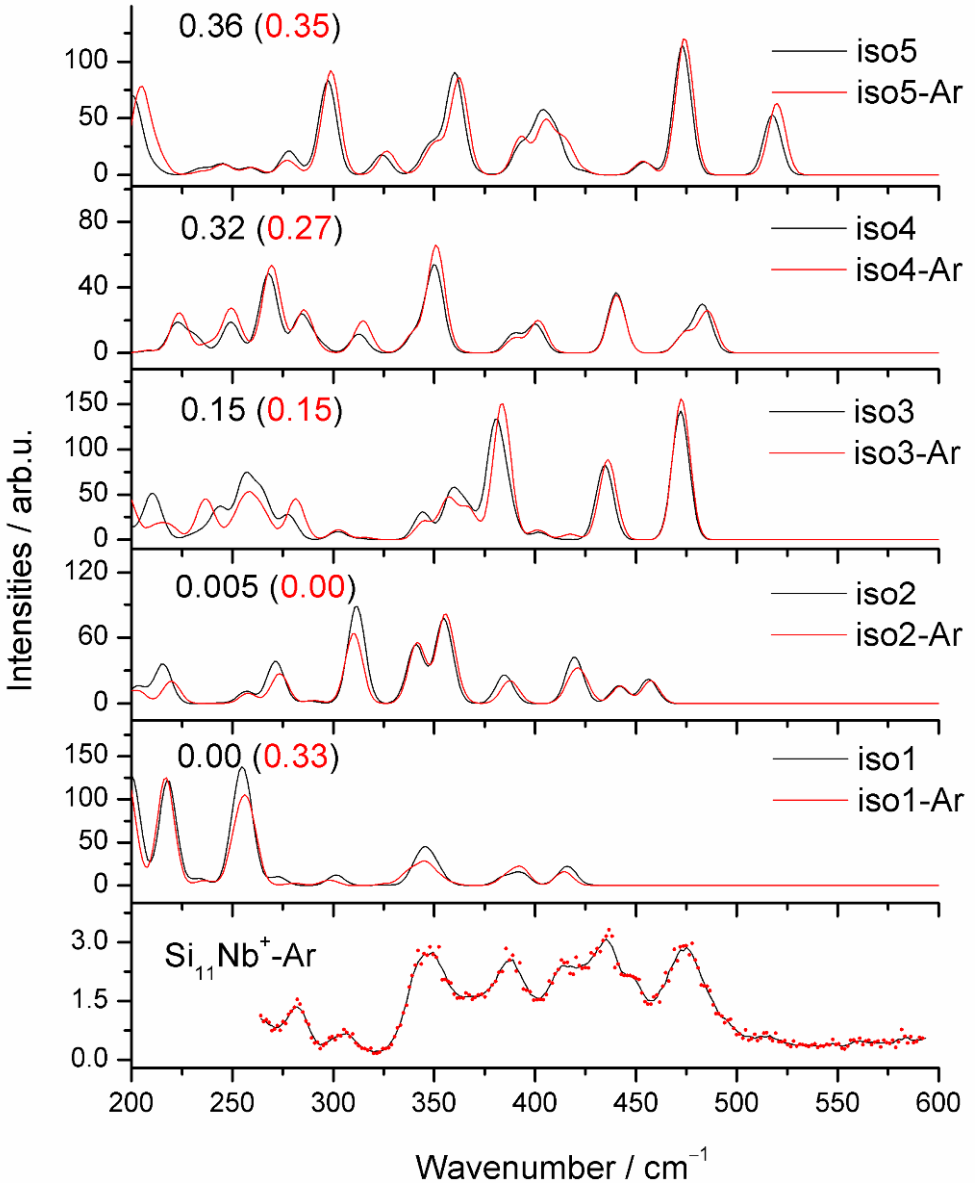
Cluster	NCP on Nb atom (e)	NEC on Nb atom
Si_4Nb^+	0.142	[core]$4d^{4.43}5s^{0.43}5d^{0.02}6p^{0.03}$
Si_5Nb^+	0.091	[core]$4d^{4.41}5s^{0.47}5d^{0.02}6p^{0.05}$
Si_6Nb^+	–0.165	[core]$4d^{4.64}5s^{0.48}5d^{0.03}6p^{0.06}$
Si_7Nb^+	–0.178	[core]$4d^{4.69}5s^{0.43}5p^{0.02}5d^{0.03}6p^{0.05}$
Si_8Nb^+	–0.406	[core]$4d^{4.89}5s^{0.43}5p^{0.06}5d^{0.04}6p^{0.03}$
Si_9Nb^+ iso1	–0.408	[core]$4d^{4.89}5p^{0.06}6s^{0.44}5d^{0.04}6p^{0.03}$
Si_9Nb^+ iso2	–0.654	[core]$4d^{5.11}5p^{0.06}6s^{0.44}5d^{0.04}6p^{0.04}$
$Si_{10}Nb^+$ iso1	–0.722	[core]$4d^{5.21}5p^{0.07}6s^{0.43}5d^{0.04}6p^{0.01}$
$Si_{10}Nb^+$ iso2	–0.623	[core]$4d^{5.09}5s^{0.44}5p^{0.03}5d^{0.05}6p^{0.05}$
$Si_{10}Nb^+$ iso3	–0.944	[core]$4d^{5.40}5s^{0.45}5p^{0.08}5d^{0.04}6p^{0.01}$
$Si_{11}Nb^+$ iso1	–1.160	[core]$4d^{5.58}5s^{0.43}5p^{0.05}5d^{0.09}6p^{0.04}$
$Si_{11}Nb^+$ iso2	–1.003	[core]$4d^{5.46}5p^{0.09}6s^{0.43}5d^{0.05}6p^{0.01}$
$Si_{11}Nb^+$ iso3	–0.885	[core]$4d^{5.37}5s^{0.41}5p^{0.06}5d^{0.04}6p^{0.03}$
$Si_{12}Nb^+$	–1.034	[core]$4d^{5.48}5p^{0.01}6s^{0.01}5d^{0.06}6p^{0.07}7s^{0.44}$



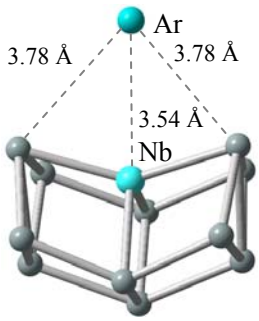
(a) Si_9Nb^+ cluster



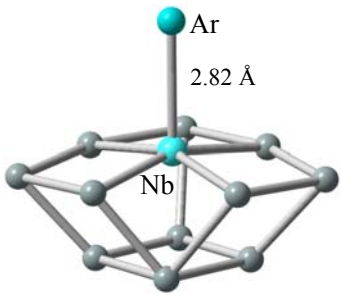
(b) $Si_{10}Nb^+$ cluster



(c) $Si_{11}Nb^+$ cluster



iso1



iso2

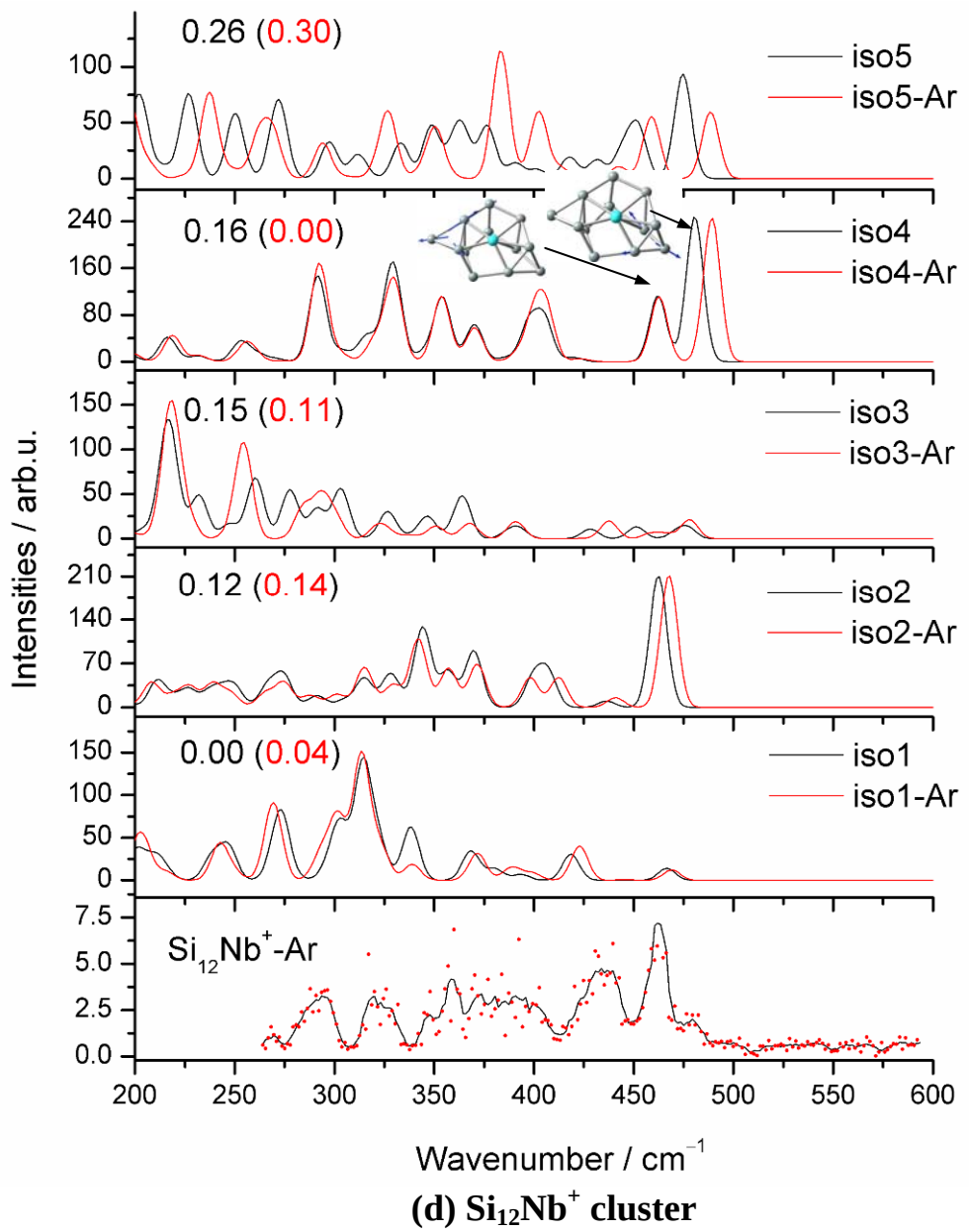


Figure S1. The bottom panels show the experimental IR-MPD spectrum of Si_nNb^+-Ar (n = 9-12). The upper panels show the (scaled) IR spectra of the low-lying isomers of Si_nNb^+ (n = 9-12) and their Ar complexes as calculated at the BP86/def-SVP level of theory. The relative energies without (black) and with (red) Ar atom are given also. Calculated spectra are convoluted by a Gaussian line shape with a full width at half-maximum (FWHM) of 10 cm^{-1}. The scaling factor of 1.04 was applied to correct all calculated vibrational spectra.

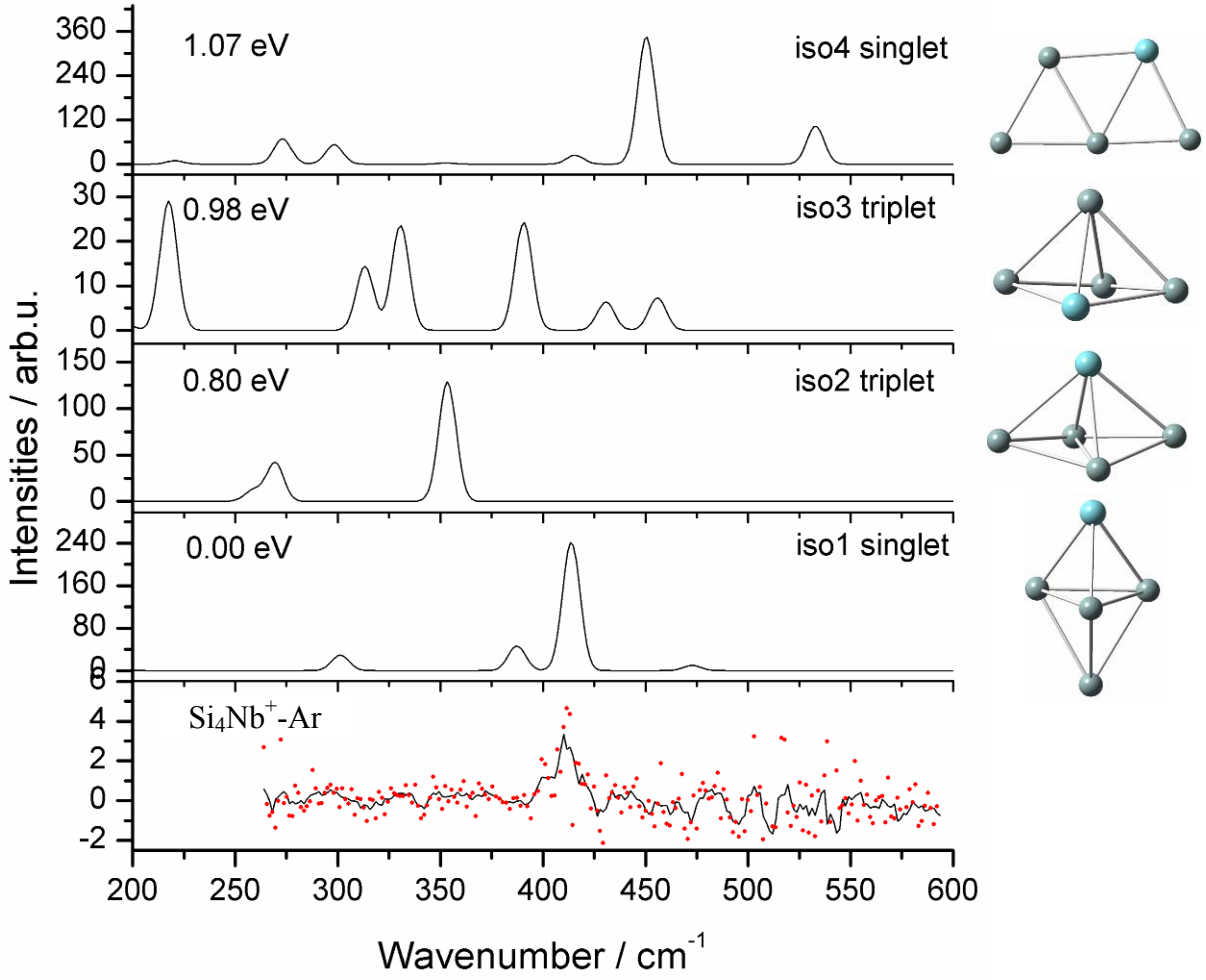


Figure S2. Comparison of experimental IR-MPD spectrum (lower) of Si_4Nb^+-Ar and the corresponding calculated IR spectra (upper) of the low-lying isomers. The relative energies obtained at the BP86/def-SVP level of theory were given.

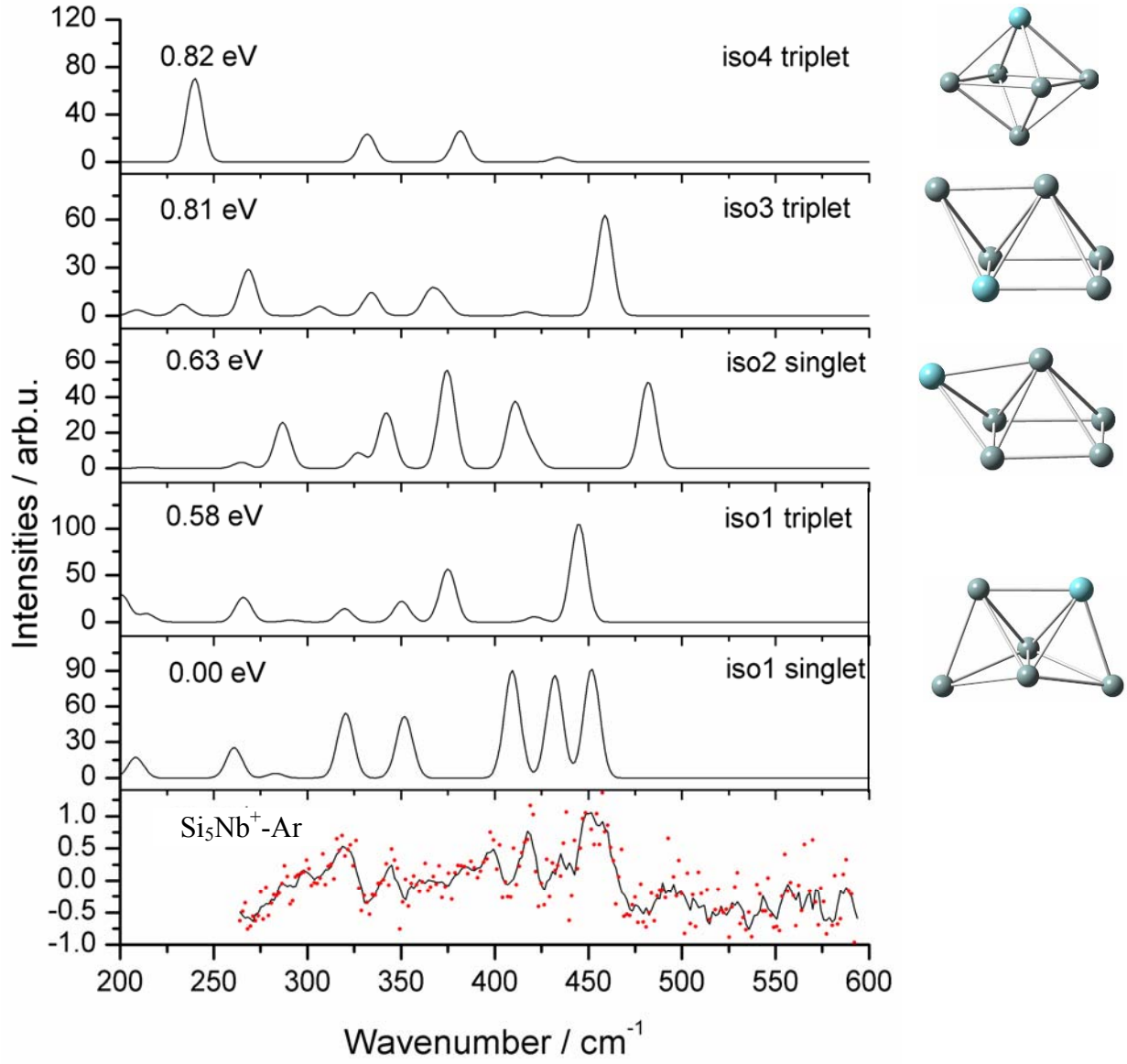


Figure S3. Comparison of experimental IR-MPD spectrum (lower) of Si_5Nb^+-Ar and the corresponding calculated IR spectra (upper) of the low-lying isomers. The relative energies are given at the BP86/def-SVP level of theory .

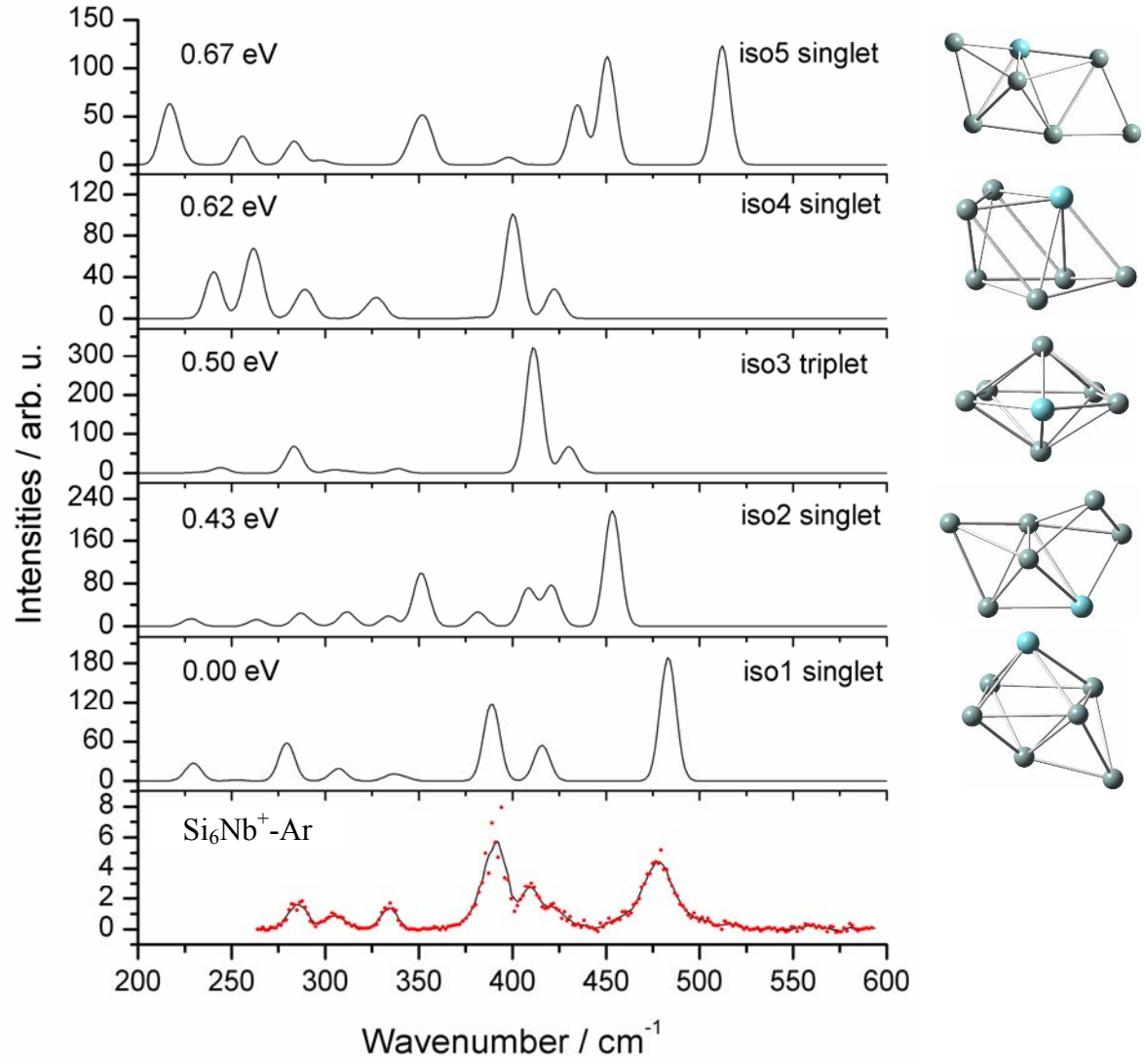


Figure S4. Comparison of experimental IR-MPD spectrum (lower) of Si_6Nb^+-Ar and the corresponding calculated IR spectra (upper) of the low-lying isomers. The relative energies obtained at the BP86/def-SVP level of theory are given.

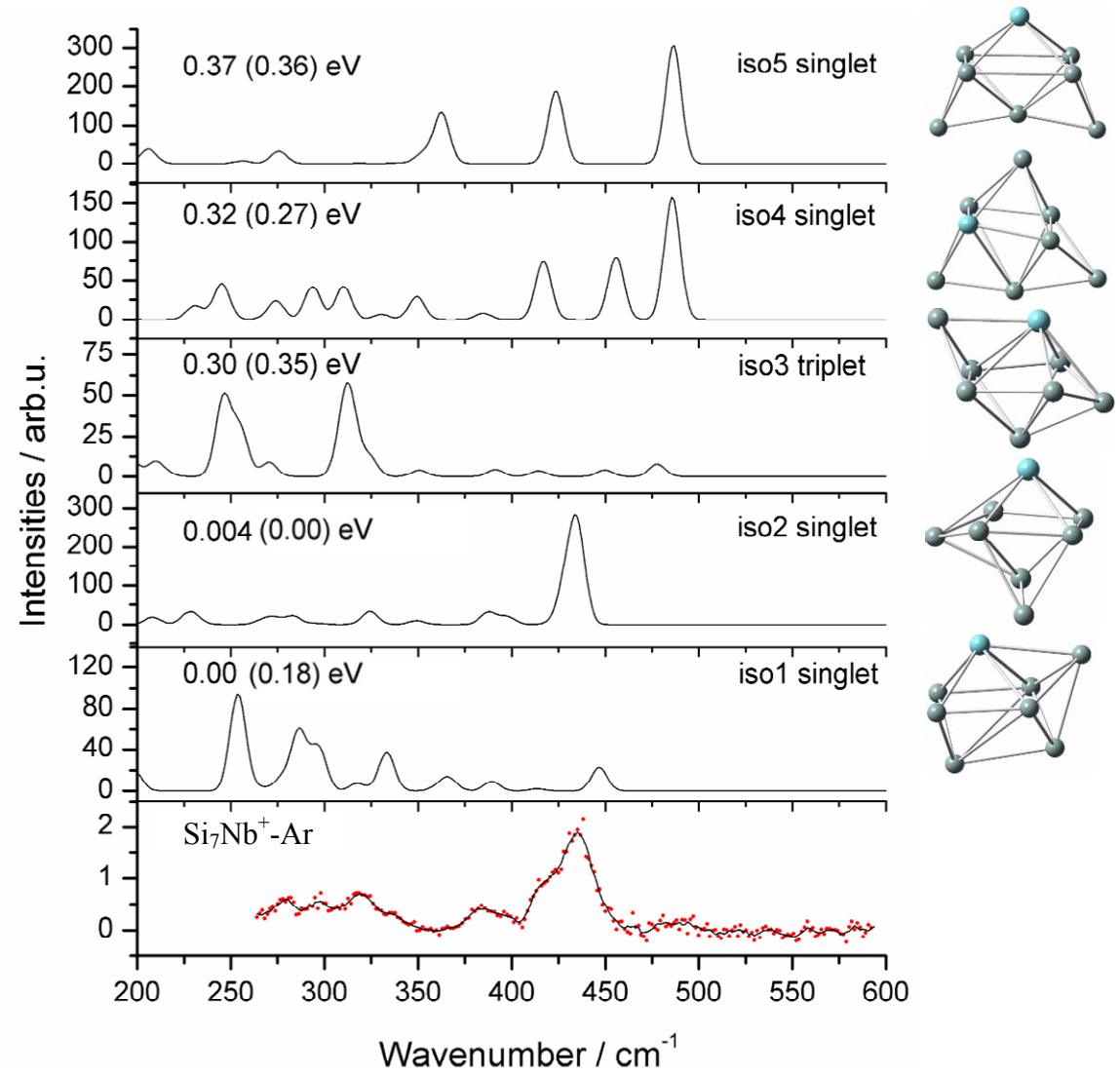


Figure S5. Comparison of experimental IR-MPD spectrum (lower) of Si_7Nb^+-Ar and the corresponding calculated IR spectra (upper) of the low-lying isomers. The relative energies are calculated at the BP86/def-SVP level of theory and at the B3LYP/def-SVP level (in parentheses).

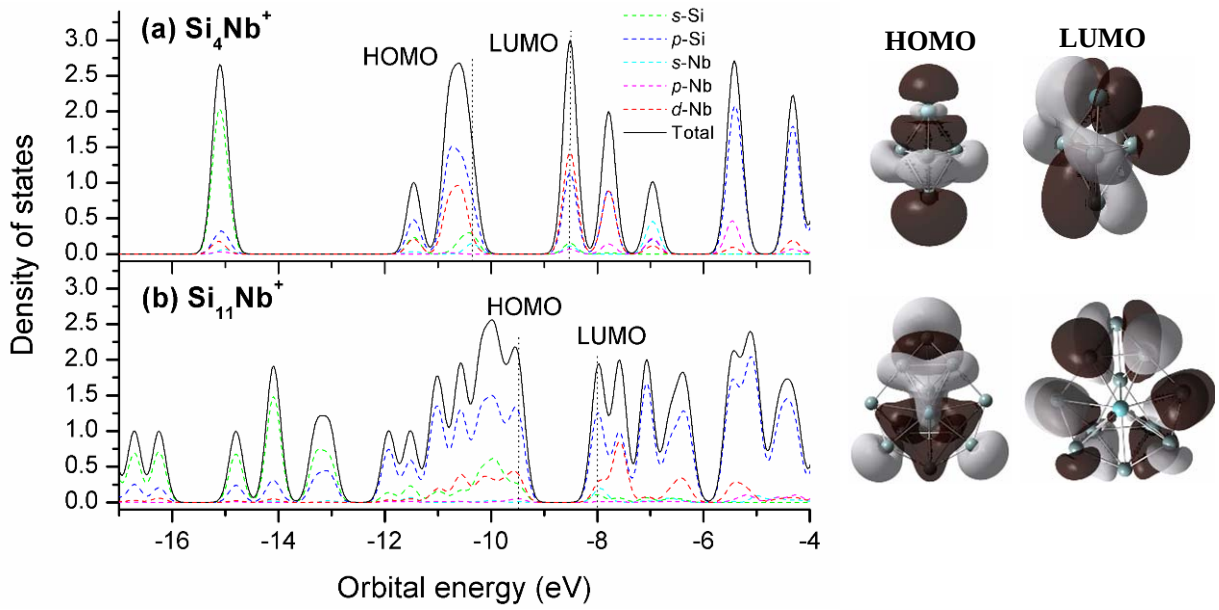


Figure S6. Total density of states (DOS) and partial density of states (PDOS) of (**a**) Si_4Nb^+ and (**b**) $Si_{11}Nb^+$ obtained at the BP86/def-SVP level of theory. The shapes of the HOMO and LUMO for those two clusters (isovalue = 0.02) are shown on the right.

Table S4. Cartesian coordinates (in Å) of the four lowest energy isomers of Si_4Nb^+.

iso1 singlet

Nb, 0. , -0. 0000000014, -1. 4121149269
Si, 0. , -0. 0000000014, 2. 5768155479
Si, -0. 0000000032, 1. 4397931085, 0. 5111268415
Si, -1. 2468974078, -0. 7198965592, 0. 5111268415
Si, 1. 246897411, -0. 7198965537, 0. 5111268415

iso2 triplet

Nb, 0. , 0. , 1. 0702147263
Si, 1. 4118726444, 0. , -0. 954359202
Si, 0. , 1. 9630206038, -0. 6236194563
Si, 0. , -1. 9630206038, -0. 6236194563
Si, -1. 4118726444, 0. , -0. 954359202

iso3 triplet

Nb, 0. 2040368806, 1. 1762673132, 0.
Si, 0. 2107910332, -0. 5221654579, -1. 791762093
Si, -1. 6461696367, -0. 4066030871, 0.
Si, 0. 5813074996, -1. 9368201103, 0.
Si, 0. 2107910332, -0. 5221654579, 1. 791762093

iso4 singlet

Nb, 1. 1498526534, 0. 6563228031, 0.
Si, 1. 4856545777, -1. 737496669, 0.
Si, -2. 9629448527, -0. 3453214983, 0.
Si, -1. 1835632264, 1. 2582718897, 0.
Si, -0. 704165622, -1. 1061689055, 0.

Table S5. Cartesian coordinates (in Å) of the five low-lying isomers of Si_5Nb^+.

iso1 singlet

Nb, -1. 3068401126, 0. 5696689633, 0.
Si, 0. 591563625, -0. 5486084228, -1. 237894662
Si, 0. 9520874898, 1. 5787749602, 0.
Si, 0. 591563625, -0. 5486084228, 1. 237894662
Si, -1. 0309917396, -1. 8998889507, 0.
Si, 2. 7065452623, -0. 2536769712, 0.

iso1 triplet

Nb, 1. 3616738174, -0. 4808332162, 0.
Si, -0. 6235279753, 0. 5230888809, 1. 2971489399
Si, -0. 8069174659, -1. 6532207728, 0.
Si, -2. 6197842142, -0. 0131409472, 0.
Si, 0. 6553455685, 2. 0745010328, 0.
Si, -0. 6235279753, 0. 5230888809, -1. 2971489399

iso2 singlet

Nb, 0. 0696264527, -1. 7262302984, 0.
Si, -0. 8465000523, 0. 0466665418, -1. 2977119251

Si, 0.0162167753, 2.3087751335, 1.2295805091
Si, 0.0162167753, 2.3087751335, -1.2295805091
Si, -0.8465000523, 0.0466665418, 1.2977119251
Si, 1.251024114, 0.4260886767, 0.
iso3 triplet
Nb, 0.0279164367, 0.6897201706, 0.7335749932
Si, -0.1813105139, -0.1102058236, -1.5634186236
Si, 1.048638338, -2.0169070465, -0.8383711126
Si, 1.3746998026, -1.3231087918, 1.451275726
Si, -0.9939739859, -1.7230998874, 0.3548557244
Si, -0.7369600776, -0.9239986215, 2.5570652927
iso4 triplet
Nb, 1.1677090842, 0.7106163661, -0.1196074392
Si, -0.2097659523, -0.8704848617, 1.2886097837
Si, -0.3733976274, 0.573847583, -2.0080232822
Si, 0.6077062112, -1.6903183958, -1.0846502472
Si, -1.6203655124, -0.9516438056, -0.6693955467
Si, 2.0603047967, -1.5118078859, 0.7626287316

Table S6. Cartesian coordinates (in Å) of the five low-lying isomers of Si_6Nb^+.
iso1 singlet
Nb, -1.2972788352, -0.6910892737, 0.
Si, -0.8556935648, 1.2790230898, -1.4895961026
Si, 0.8215652827, -0.8878850198, -1.2546937231
Si, 1.0024261426, 1.3579676736, 0.
Si, -0.8556935648, 1.2790230898, 1.4895961026
Si, 0.8215652827, -0.8878850198, 1.2546937231
Si, 2.8651902468, -0.11775463, 0.
iso2 singlet
Nb, -0.0659701647, 0.4980741569, 0.9375340254
Si, -1.9422078773, 1.1062337059, -0.6529797838
Si, -1.0152171001, 1.9757287779, -2.8131920913
Si, -1.6590101938, 2.9955105835, 0.8477961623
Si, 0.5992988373, 2.7536811059, 1.7149231665
Si, 0.1885307744, 0.1737905024, -1.491505227
Si, 0.1417417242, 2.5476181676, -0.7493122523
iso3 triplet
Nb, 0., 0., -1.79743245
Si, 0., 1.34655201, 2.23054855
Si, -1.322551, 0., 0.57068055
Si, 0., -1.908459, -0.16927445
Si, 1.322551, 0., 0.57068055
Si, 0., -1.34655201, 2.23054855
Si, 0., 1.908459, -0.16927445

iso4 singlet

Nb, -1.0521750569, -0.5114856921, 0.

Si, -0.7352653365, 1.5724000798, -1.3179981331

Si, 1.2756552348, -0.4240231354, -1.4045000042

Si, -0.7352653365, 1.5724000798, 1.3179981331

Si, 1.2756552348, -0.4240231354, 1.4045000042

Si, 1.2758464027, 1.5157046577, 0.

Si, 0.724470905, -2.3143858919, 0.

iso5 singlet

Nb, 0.6927608211, 0.9223746531, 0.682732811

Si, -0.825825526, 0.4327969498, -1.6664877053

Si, -1.3606797128, 0.9064708774, 2.0748643487

Si, -1.3045790499, 2.2030732091, -0.1567559007

Si, 0.8981388498, -0.4225309375, -3.0260952706

Si, 0.9974116841, -1.0123584788, -0.7560201255

Si, -1.7576300662, -0.5110692731, 0.2674688424

Table S7. Cartesian coordinates (in Å) of the five low-lying isomers of Si_7Nb^+.

iso1 singlet

Nb, 1.2054177771, 0.1575557602, 0.

Si, 0.3692760062, -1.4387529091, 1.7773558054

Si, -0.5375062798, 0.6939866781, 1.9346969435

Si, -1.1939329802, -1.7353034683, 0.

Si, -0.5375062798, 0.6939866781, -1.9346969435

Si, 0.3692760062, -1.4387529091, -1.7773558054

Si, -1.942022686, 0.6839112778, 0.

Si, -0.1386498136, 2.3217989523, 0.

iso2 singlet

Nb, 0.5862261882, 1.6253681716, 1.3340207306

Si, 1.2537485736, 0.6990486538, -0.9329815078

Si, -0.2412054646, -1.1918830896, -1.5986899677

Si, -1.078989877, 0.5984084742, -0.118547021

Si, 2.8329093242, -0.3288906296, 0.5322941128

Si, -0.6085714218, -0.1224861337, 2.6317261766

Si, 1.8559835712, -0.333694276, 2.7006228008

Si, 0.5138281064, -1.2531251706, 0.7544726756

iso3 triplet

Nb, 1.1989964583, -0.0753434068, 0.

Si, 0.0525953201, 0.9323552119, -2.0708625833

Si, -0.0680061624, 2.313826375, 0.

Si, -0.971937407, -1.0913299634, -1.4767857932

Si, 0.0525953201, 0.9323552119, 2.0708625833

Si, 0.1890532842, -2.4798929817, 0.

Si, -0.971937407, -1.0913299634, 1.4767857932

Si, -1. 8026464964, 0. 7095586666, 0.
iso4 singlet
Nb, -0. 1178443601, 0. 604511808, 0. 9281567721
Si, 0. 7505234675, -1. 7243939681, 0. 3631263824
Si, -1. 740328754, -1. 3579601981, 0. 512059187
Si, 0. 2955180029, -0. 4893219824, -1. 5587481355
Si, -0. 8577004991, 0. 778872748, -3. 3055628241
Si, -2. 2198876203, 0. 0288355446, -1. 4295498871
Si, -2. 4957902857, 1. 3702344971, 0. 489891812
Si, -0. 437810951, 1. 8859625508, -1. 1545063067
iso5 singlet
Nb, 0. , 0. , -1. 5773169399
Si, -1. 2675209755, 1. 5887637379, -0. 1194029221
Si, 0. , 2. 3788101917, 1. 8432204514
Si, -1. 2675209755, -1. 5887637379, -0. 1194029221
Si, 0. , -2. 3788101917, 1. 8432204514
Si, 1. 2675209755, 1. 5887637379, -0. 1194029221
Si, 1. 2675209755, -1. 5887637379, -0. 1194029221
Si, 0. , 0. , 1. 3991537034

Table S8. Cartesian coordinates (in Å) of the five low-lying isomers of Si_8Nb^+.
iso1 singlet
Nb, 0. 9055431095, 0. 5664374572, 1. 0928890301
Si, 1. 2023335619, -1. 7105802771, -0. 1932360675
Si, -0. 9601990165, -2. 7658893554, -0. 6972124864
Si, -0. 6872690533, -1. 871295626, 1. 5974372293
Si, 1. 7009669405, -1. 6775023877, 2. 4438504763
Si, -1. 6497590006, 0. 3722479147, 1. 8085812684
Si, -0. 0057998007, -0. 4243298597, 3. 4714130521
Si, 3. 1619880193, -0. 8011040275, 0. 7602227598
Si, -0. 7553587601, -0. 3027658384, -0. 5219572619
iso2 singlet
Nb, 1. 0556094416, -0. 371295033, 0.
Si, -0. 6724207995, 1. 2940614029, -1. 8390887038
Si, -1. 0018975228, -1. 5540030749, 1. 2089679786
Si, 0. 7587613976, -0. 4547650432, 2. 5389327649
Si, 0. 604835751, 2. 1047936949, 0.
Si, -0. 6724207995, 1. 2940614029, 1. 8390887038
Si, 0. 7587613976, -0. 4547650432, -2. 5389327649
Si, -1. 0018975228, -1. 5540030749, -1. 2089679786
Si, -1. 8793764934, 0. 4024877788, 0.
iso3 singlet
Nb, -0. 7547568862, 0. 8605197984, -0. 9410325604
Si, 0. 9831905211, -1. 2956660234, 1. 0651799068

Si, 3.1460000066, -0.5522930855, 0.3687905553
Si, 1.3386162075, -0.4258855438, -1.3927151668
Si, -0.6593263003, -1.8076796251, -0.5518890923
Si, 1.4397581463, 1.185452094, 0.4724702177
Si, -2.6443475598, -0.7321750629, -0.0282451724
Si, -1.1436583574, -0.2958628348, 1.7850033217
Si, -0.5713507778, 2.038165283, 1.2692549904

iso4 singlet

Nb, 0.757131336, -1.3749721323, 0.
Si, -1.1957519862, -0.0612600632, 1.3524210148
Si, -0.3813542295, 1.977097615, 2.3653104102
Si, 1.2592821095, 0.2527164172, 1.7989932844
Si, -1.1957519862, -0.0612600632, -1.3524210148
Si, -1.8077382437, -1.892177159, 0.
Si, -0.3813542295, 1.977097615, -2.3653104102
Si, 0.2298648539, 1.5715593797, 0.
Si, 1.2592821095, 0.2527164172, -1.7989932844

iso5 singlet

Nb, 0.3482871877, 1.3612138059, 0.
Si, -1.0066919896, -0.2781825255, 1.6910341362
Si, 2.6195365066, -1.140612815, 0.
Si, 1.3026330659, -0.0383815556, 1.8510172798
Si, 0.3094765184, -1.5668503258, 0.
Si, -1.0066919896, -0.2781825255, -1.6910341362
Si, -2.3316230501, -1.6473944684, 0.
Si, -2.1988741151, 1.0254366956, 0.
Si, 1.3026330659, -0.0383815556, -1.8510172798

Table S9. Cartesian coordinates (in Å) of the five low-lying isomers of Si_9Nb^+.

iso1 singlet

Nb, 0.7596944337, 0.1726515044, 0.9822437344
Si, 0.6475688644, 1.4851426335, -1.1267987524
Si, -1.6558965766, 0.4745966647, 1.9256904137
Si, -1.1102523556, 0.9265057794, -2.763246999
Si, -2.8232771366, -1.7864874243, 2.2941022617
Si, -1.5798398616, 0.7732571394, -0.3997415201
Si, 0.8674998637, -2.3163552033, 0.3018824103
Si, -0.3804014464, -1.5783621191, 2.4733124167
Si, -1.5680117263, -1.6298357883, 0.2559562768
Si, 0.0534069411, -0.9456631864, -1.494473242

iso2 singlet

Nb, 1.7676535154, 0.8441029483, 0.2245554321
Si, -0.7139276969, -0.3020529698, -0.6383316195
Si, 0.9515665062, -1.5291166545, 0.7331339855

Si, 1.6885066085, -0.9190413692, -1.5876728587
Si, 1.6237701718, -0.2201567943, 2.7331193554
Si, 0.7390533071, 2.0151224476, 2.2856062536
Si, 0.4211514556, 1.449391308, -1.9376720039
Si, -0.1539677, -2.5841138378, -1.2720131744
Si, -0.7506134906, 0.0633203728, 1.8641277852
Si, -0.6897316772, 2.0592525489, 0.2358398447

iso3 singlet
Nb, 1.1695191286, 0.4736910088, 0.
Si, 0.8057922381, -1.7463817646, 1.2149597958
Si, -1.8722025727, 1.3626310587, 0.
Si, -0.627328323, 0.1707945699, 2.0491894153
Si, 0.0530715716, 2.4276386404, 1.2864593749
Si, -1.3499737078, -1.0689449456, 0.
Si, 0.8057922381, -1.7463817646, -1.2149597958
Si, -0.627328323, 0.1707945699, -2.0491894153
Si, -0.6827178437, -3.3808911225, 0.
Si, 0.0530715716, 2.4276386404, -1.2864593749

iso4 singlet
Nb, 0.10932173, 0.8364063245, 1.106746733
Si, -0.4029002195, -1.7015388933, 0.6553123225
Si, -0.6153510901, 0.6660493013, -3.3963476402
Si, -0.1896993227, 1.9158358037, -1.314953082
Si, 0.1021635598, -0.7044674187, -1.4641040203
Si, -2.2073926241, -0.3250448519, 0.4198050274
Si, -2.4780682606, 0.9120667614, -1.9883836024
Si, -4.0530510089, 1.0530342793, -0.2559561153
Si, -1.944018317, 2.0826264709, 0.4772437358
Si, 1.8304905532, 0.8340592229, -0.7192333584

iso5 singlet
Nb, 1.4289536196, 0.5378092103, 0.3957061987
Si, -2.7361750912, 1.927732122, -0.0624055198
Si, -0.3497244498, 2.4241788573, 0.9674751434
Si, 0.0829336565, -0.9418466155, -1.2161590874
Si, -0.7715828149, 1.5102834463, -1.5115408212
Si, 1.3158179858, 0.9632405761, -2.3271996517
Si, -1.145010377, -0.0769823219, 0.6097331754
Si, -2.2134260191, 1.4222328736, 2.3093786124
Si, 0.1502083801, 0.6248953024, 2.6295519707
Si, 1.2952941102, 2.8710325494, -0.6708080207

Table S10. Cartesian coordinates (in Å) of the five low-lying isomers of $Si_{10}Nb^{+}$.

iso1 singlet
Nb, 0.9388523824, -0.2232777824, 0.

Si, 0.0278179142, 2.1040818405, 2.3615879776
Si, -0.8254269969, -1.7888549013, 1.7819730988
Si, 0.3419483097, -2.8159333209, 0.
Si, -1.4850787476, 0.4710327868, 1.2341986441
Si, -1.4850787476, 0.4710327868, -1.2341986441
Si, 0.1026889608, 2.2710610682, 0.
Si, 0.6722338395, -0.2036193141, 2.5704275728
Si, 0.0278179142, 2.1040818405, -2.3615879776
Si, 0.6722338395, -0.2036193141, -2.5704275728
Si, -0.8254269969, -1.7888549013, -1.7819730988
iso2 singlet
Nb, 1.0061644516, 0.5094155656, 0.7841628245
Si, -0.2151415463, -1.325753022, -0.5967593519
Si, 2.5101616008, -0.8888730453, 2.2825777601
Si, 0.1269451452, 0.9283336308, -1.5633576691
Si, -1.6593502629, 0.6438149483, 0.1994520967
Si, -1.9318457003, -0.2484046973, -2.0911569946
Si, -3.0944903228, 0.3801537285, 2.1190305872
Si, -0.7472914548, 1.3176221902, 2.4608481476
Si, -1.2386411855, -1.1553896472, 2.0455296889
Si, 0.5613231032, -0.4195912638, 3.5395091917
Si, 0.7745001718, -2.3495273878, 1.285011719
iso3 singlet
Nb, -0.016689, 0.105611, 0.943219
Si, -1.696786, 2.086814, 0.731243
Si, -0.409506, 1.774712, -1.263641
Si, -1.823781, -1.741139, 0.806857
Si, 1.315526, -0.002506, -1.535835
Si, -2.773559, 0.173994, -0.184229
Si, 1.803037, -1.706107, 0.685837
Si, 3.099149, 0.184677, 0.103607
Si, -0.057595, -2.504705, -0.562588
Si, -1.010265, -0.634941, -1.773517
Si, 1.602655, 2.059912, 0.229982
iso4 singlet
Nb, 1.5453298265, 0.7518961986, 0.2581290487
Si, -0.3020474153, 0.1314363047, 1.9696334274
Si, -1.2471586151, 0.9106463805, -0.584021528
Si, -0.303972098, -1.4294081174, -0.2366228489
Si, 0.8647252215, -1.9213473826, 1.9078028157
Si, 2.2130506821, -1.7880205908, -0.1122456259
Si, 0.1823544882, 1.6689992361, -2.4258947309
Si, 1.2963985836, -0.4327594898, -1.9639534678
Si, -1.0277274647, 2.3227946271, 1.4184144153

Si, 0.4056672656, 2.9217778531, -0.4561816897
Si, 0.9206485256, -2.7849570196, -1.9937198159
iso5 singlet
Nb, -1.2538089255, -1.1713429421, 0.
Si, -0.5843563732, 3.6532124914, 0.
Si, 1.2832044661, -1.7003648245, 1.4130808168
Si, -0.2832339924, 0.0964290455, -1.9400468215
Si, -1.1693366273, 1.4392759453, 0.
Si, -0.2832339924, 0.0964290455, 1.9400468215
Si, 0.174986769, -3.254617551, 0.
Si, 0.9119014881, 2.2593491675, -1.4890938805
Si, 1.2832044661, -1.7003648245, -1.4130808168
Si, 1.4400272834, 0.2745100995, 0.
Si, 0.9119014881, 2.2593491675, 1.4890938805

Table S11. Cartesian coordinates (in Å) of the five low-lying isomers of $Si_{11}Nb^+$.
iso1 singlet
Nb, 0., 0., 0.7410137145
Si, -2.1902641161, 1.9435748134, 0.2065746844
Si, -2.3504290861, 0., -1.158456595
Si, -2.1902641161, -1.9435748134, 0.2065746844
Si, 2.1902641161, -1.9435748134, 0.2065746844
Si, 2.1902641161, 1.9435748134, 0.2065746844
Si, 0., 0., -2.1404757786
Si, 2.3982098097, 0., 1.5555528281
Si, 2.3504290861, 0., -1.158456595
Si, 0., 2.0574323225, -0.8113976798
Si, 0., -2.0574323225, -0.8113976798
Si, -2.3982098097, 0., 1.5555528281
iso2 singlet
Nb, 0.1173331557, -0.2633468017, 1.0407266456
Si, -1.7403459531, 1.4956387993, 1.2720387042
Si, 2.0130431313, 1.4501306646, 1.1099314257
Si, -1.5505583626, 0.2705662575, -1.1758001587
Si, 0.5762259441, -3.2032008914, -0.3597059776
Si, 2.2364564958, -1.4498630877, 0.2432321608
Si, -1.4630151499, -2.103951709, 0.1962373244
Si, -3.0902124126, -0.4168811665, 0.7275752196
Si, 0.0682577698, 1.9715953796, -0.6927018419
Si, 0.3103488979, -1.1704761415, -1.6317329959
Si, 2.0053926388, 0.5321972654, -1.1344774263
Si, 0.0987771349, 2.9939652416, 1.4923693003
iso3 singlet
Nb, 0.9753630931, -0.3053006788, 0.

Si, -1.6350701267, -0.9317917337, -1.2813533698
Si, 0.5678963579, -1.8859336975, -2.0372760463
Si, 0.0850644154, 0.3281639894, -2.7507950659
Si, -1.6350701267, -0.9317917337, 1.2813533698
Si, -0.7673901172, 3.5384172788, 0.
Si, 0.5678963579, -1.8859336975, 2.0372760463
Si, 0.0850644154, 0.3281639894, 2.7507950659
Si, -1.3141984402, 1.1312012903, 0.
Si, -0.3445358734, -2.8556960723, 0.
Si, 0.7786788449, 2.0242851448, -1.2119636433
Si, 0.7786788449, 2.0242851448, 1.2119636433

iso4 singlet

Nb, 1.1162032251, 1.5452389168, 0.
Si, -1.605585432, 0.4907309245, 0.
Si, -1.5913195688, 2.8388537835, 0.
Si, 0.2593404197, -0.3864652749, 1.6104711608
Si, 0.2593404197, -0.3864652749, -1.6104711608
Si, -0.5189254325, 1.780111101, 1.9700798126
Si, -1.6998009096, -1.9758731444, 0.
Si, -0.4701463568, -2.6376560122, -2.026673327
Si, -0.5189254325, 1.780111101, -1.9700798126
Si, -0.4701463568, -2.6376560122, 2.026673327
Si, 2.2267822669, -0.6657239317, 0.
Si, 0.8107574351, -2.729631891, 0.

iso5 singlet

Nb, -0.3152394566, 0.2572255096, 0.8965791819
Si, -2.1755250679, -1.5014173157, 0.3364422897
Si, -1.1978848929, 2.501250376, -0.0914483441
Si, -0.2358371967, -1.0235741001, -1.5773210427
Si, 1.7550972007, 0.2841905282, -1.3475439976
Si, 2.2168091721, 0.8049339039, 1.0847259068
Si, -0.3409544002, -2.926721189, -0.0222861171
Si, 1.1919775547, 2.459557928, -0.3421467857
Si, 1.5695799785, -1.4887926968, 0.4747907618
Si, 3.7211436786, -0.7147835478, -0.2146455332
Si, -3.6876164701, 0.2207529392, 0.2820965895
Si, -1.9294291003, 0.5896106644, -1.2607819091

Table S12. Cartesian coordinates (in Å) of the five low-lying isomers of $Si_{12}Nb^{+}$.

iso1 singlet

Nb, -0.4828830119, -0.0779999508, 0.
Si, -0.4353156461, 0.1270319621, 2.6037393761
Si, -1.3536637952, -2.5451384424, 0.
Si, 1.3727582926, 1.3387690517, 1.7189614093

Si, 1.3727582926, 1.3387690517, -1.7189614093
Si, -0.1661791476, -2.3011116582, -1.980402327
Si, 0.5552276446, 2.8024988857, 0.
Si, -1.365021731, 2.0831533415, 1.3216352004
Si, -0.1661791476, -2.3011116582, 1.980402327
Si, 2.165750707, -0.129982121, 0.
Si, 1.2677450421, -2.4036430757, 0.
Si, -0.4353156461, 0.1270319621, -2.6037393761
Si, -1.365021731, 2.0831533415, -1.3216352004

iso2 singlet

Nb, 0.1778008686, -0.0194699736, -0.7039607246
Si, 1.4140592603, -2.3079861293, 0.17691491
Si, 0.3210473053, -0.9497388663, 2.0384591843
Si, 2.5213855384, -0.7370140913, -1.5167575325
Si, -3.9371635992, 0.4648964242, 0.2549432088
Si, -1.0467357955, -2.4149360276, -0.172651143
Si, 2.2350963246, 1.597089021, -0.6383056639
Si, 0.2212467464, 2.8981813046, -0.0678986424
Si, -2.2773510743, -0.5738611833, -1.378936404
Si, -1.8058081207, 1.5674001443, -0.3245404813
Si, 2.7899288066, -0.2425860412, 0.8841392596
Si, -1.9245886349, -0.5322939674, 1.1599384065
Si, 0.9573833743, 1.3091103859, 1.6419936225

iso3 singlet

Nb, -0.6809410054, 0.043951239, 0.
Si, 1.8214524656, 1.4987477349, 0.
Si, 0.0299649516, 2.3307176565, -1.4242950311
Si, 1.7001803528, -0.4303002375, 1.5138812532
Si, -0.0881539144, 0.3536459637, 2.8420557004
Si, -1.8190068657, 2.5169433746, 0.
Si, -1.2090773566, -2.9691698801, 0.
Si, -0.0881539144, 0.3536459637, -2.8420557004
Si, 1.7001803528, -0.4303002375, -1.5138812532
Si, 1.2037519323, -2.2117660144, 0.
Si, -0.6407916849, -1.7412868599, 1.9568836488
Si, -0.6407916849, -1.7412868599, -1.9568836488
Si, 0.0299649516, 2.3307176565, 1.4242950311

iso4 singlet

Nb, 0.7000422362, -1.1331038154, 0.708060256
Si, -2.4548775302, 0.2171137674, 3.2559156987
Si, 0.0987200769, -0.9636844775, -1.7575601326
Si, -1.5868273167, -1.6599153926, 1.8274459477
Si, 1.9553996328, -0.2037402956, -3.2222276068

Si, 1.6437105954, 0.7937021141, -1.0435458675
Si, 2.2368018561, 0.4447047513, 2.7083901474
Si, -0.0860316726, -0.2070331839, 3.0330095198
Si, 3.2226848473, -0.1095178472, 0.5864555101
Si, 2.391267595, -1.722821244, -1.1911729691
Si, -1.9866156769, -0.919384362, -0.5003086245
Si, 0.8868059114, 1.6836476066, 1.0491849023
Si, -1.4104535548, 0.8375313788, 1.0621662184

iso5 singlet

Nb, 0.1303395418, 0.3006625016, 0.3653278116
Si, 0.1555280278, -0.3383350859, 3.3452348762
Si, -1.911609143, -1.2591040017, -1.6986211663
Si, 1.5921619441, -1.4118492931, -1.1216165138
Si, -1.1408116682, -1.517229985, 1.7514223284
Si, -0.3613722721, -2.5139510831, -0.277051199
Si, -1.8954981657, 0.2665752803, -3.5416011486
Si, 1.9323271532, -1.4732639894, 2.2797795928
Si, 1.8390530729, 1.1198111146, 2.1357955465
Si, 0.1951321337, 0.1152266401, -2.2616344583
Si, 2.8817043483, -0.2608003433, 0.4744776976
Si, -2.6182058833, -0.2568193562, 0.3632332324
Si, -1.6275590893, 1.355655601, -1.2407495996