Electronic transitions in Rb_2^+ dimers solvated in helium

Simon Albertini,[1] Paul Martini,[1] Arne Schiller,[1] Harald Schöbel,[1] Elham Ghavidel,[1] Milan Ončák,[1] Olof Echt,[1,2] and Paul Scheier[1]

[1] Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, A-6020 Innsbruck, Austria

[2] Department of Physics, University of New Hampshire, Durham NH 03824, USA

Corresponding authors: Milan Ončák <Milan.Oncak@uibk.ac.at>, Olof Echt <Olof.Echt@unh.edu>

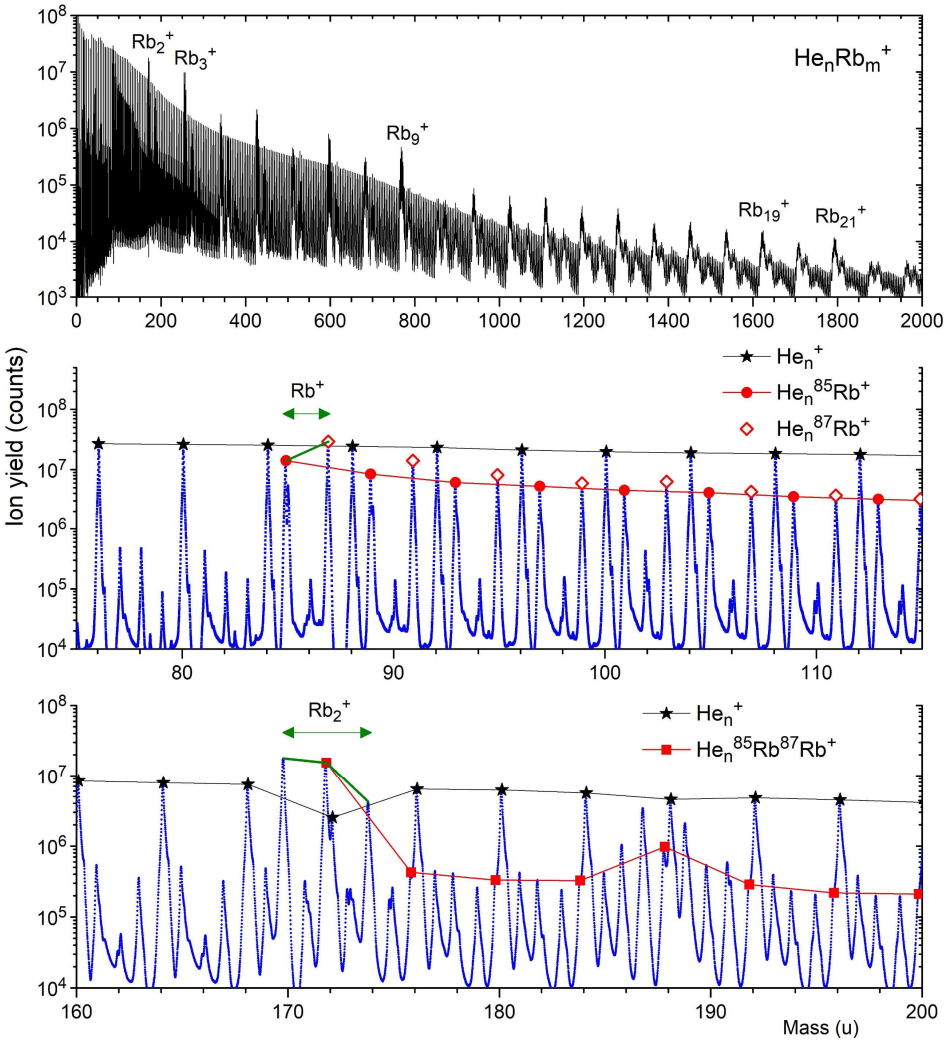

Fig. S1

Sections of a mass spectrum of HNDs doped with rubidium. This is the cumulative laser-off spectrum recorded while scanning the laser from 620 to 660 nm. The amplitudes of some mass peaks, including $^{85}Rb^+$ and He_{43}^+ (172 u) are suppressed because of deadtime effects. The $He_4{}^{85}Rb^{87}Rb^+$ peak at 188 u coincides with the $H_2O^{85}Rb_2^+$ peak.

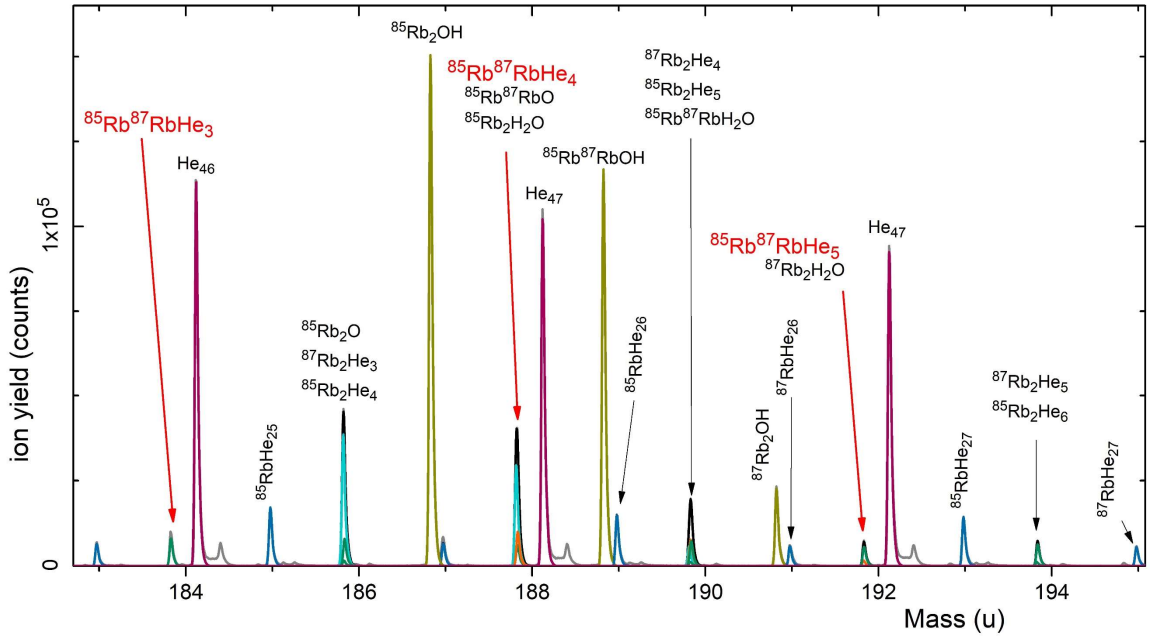

Fig. S2
A high-resolution mass spectrum of HNDs doped with rubidium.

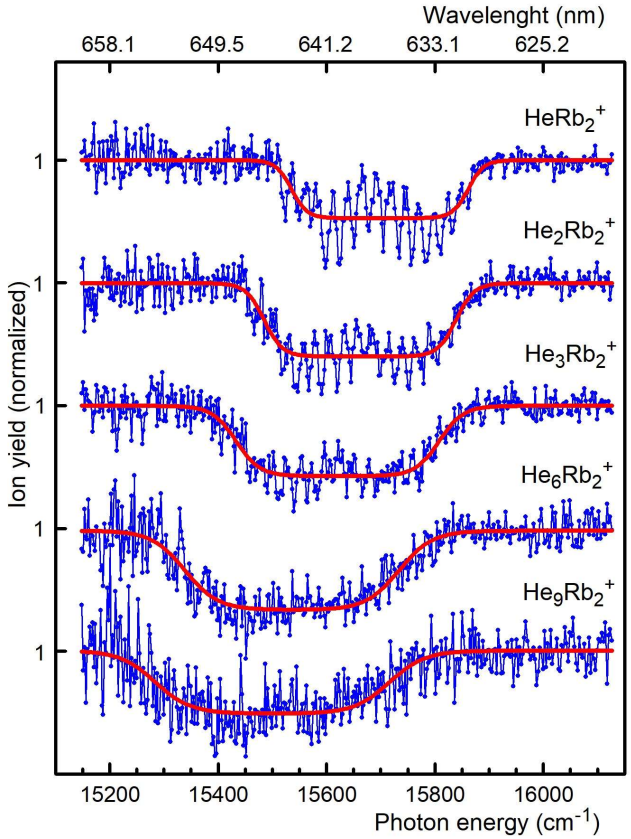

Fig. S3
High-resolution depletion spectra of $He_nRb_2^+$ for n = 1, 2, 3, 6, and 9. Vibrational structure is resolved for $n \leq 3$. The solid lines result from fitting a square function to each spectrum.

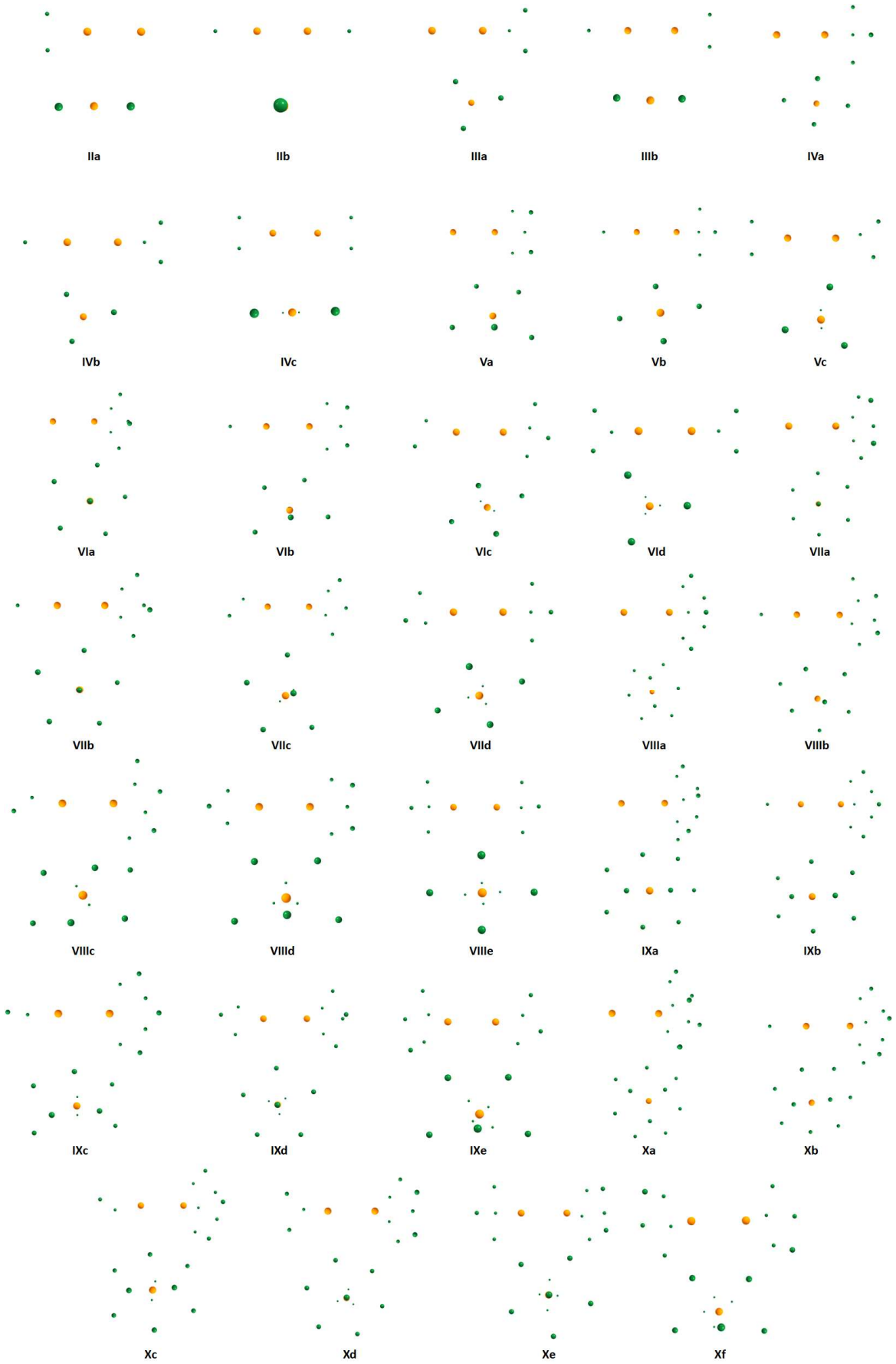

Fig. S4

Structures of $He_nRb_2^+$, $2 \leq n \leq 10$, clusters viewed from the side (above) and along the Rb-Rb axis (below). Optimized at the CCSD/def2QZVPPD(Rb),def2TZVP(He) level within frozen core approximation.

Table S1 – Properties of Rb_2^+ and $HeRb_2^+$ in the $1^2\Sigma_g^+$ electronic ground state, $1^2\Sigma_u^+$ state, and $1^2\Pi_u$ state without considering spin-orbit coupling: Equilibrium Rb-Rb and Rb-He internuclear distance r, dissociation energies D_0, harmonic constant ω_e for the Rb-Rb stretch, and transition energies (T_e and T_0 for $1^2\Sigma_u^+$ and $1^2\Pi_u$, respectively). Calculated using the (EOM)CCSD method with various basis sets. Calculated excitation energies are rounded to 10 cm^{-1}.

		def2TZVP	def2TZVPPD	def2QZVP	def2QZVPPD
Rb_2^+	r(Rb-Rb), $1^2\Sigma_g^+$ [Å]	4.987	4.982	4.912	4.883
	r(Rb-Rb), $1^2\Pi_u$ [Å]	5.541	5.523	5.697	5.455
	D_0 [cm^{-1}]	5795	5833	5840	5992
	ω, $1^2\Sigma_g^+$ [cm^{-1}]	43.3	43.4	44.0	44.7
	ω, $1^2\Pi_u$ [cm^{-1}]	26.9	27.1	23.5	25.1
	T_e, $1^2\Sigma_u^+$ [cm^{-1}]	11750	11790	12120	12290
	T_0, $1^2\Pi_u$ [cm^{-1}]	15890	15880	15940	15820
$HeRb_2^+$	r(Rb-Rb), $1^2\Sigma_g^+$ [Å]	4.986	4.981	4.912	4.889
	r(Rb-He), $1^2\Sigma_g^+$ [Å]	3.812	3.628	3.638	3.435
	r(Rb-Rb), $1^2\Pi_u$ [Å]	5.537	5.521	5.696	5.452
	r(Rb-He), $1^2\Pi_u$ [Å]	3.403	3.059	3.180	3.138
	D_0 [cm^{-1}]	5757	5762	5785	5916
	ω, $1^2\Sigma_g^+$ [cm^{-1}]	44.0	43.7	44.3	43.2
	ω, $1^2\Pi_u$ [cm^{-1}]	26.7	26.9	23.2	25.0
	T_e, $1^2\Sigma_u^+$ [cm^{-1}]	11910	11980	12300	12500
	T_0, $1^2\Pi_u$ [cm^{-1}]	15840	15780	15870	15740

Cartesian coordinates of optimized structures (in Å) along with ZPE-corrected energy (in Hartree)

Rb_2^+
E= -47.492213
Rb 0.000000 0.000000 2.586182
Rb 0.000000 0.000000 -2.586182

Ia
E= -50.385302
Rb 0.000000 0.000000 -2.405130
Rb 0.000000 0.000000 2.766228
He 0.000000 0.000000 -6.680320

IIa
E= -53.278374
Rb 2.915045 0.001593 0.000012
Rb -2.255289 -0.004775 -0.000028
He -6.081730 1.793919 0.000145
He -6.123755 -1.735048 0.000152

IIb
E= -53.278392
Rb 0.000000 0.000000 2.585203
Rb 0.000000 0.000000 -2.585203
He 0.000000 0.000000 6.866261
He 0.000000 0.000000 -6.866261

IIIa
E= -56.171423
Rb 3.053131 0.000164 -0.000172
Rb -2.116316 -0.000468 0.000525
He -5.774457 1.798773 -1.030332
He -5.779410 -0.005564 2.067036
He -5.777209 -1.787578 -1.043221

IIIb
E= -56.171464
Rb 0.001282 -2.734922 0.000000
Rb 0.001282 2.434431 0.000000
He -1.785982 6.276366 0.000000
He 1.735204 6.302278 0.000000
He 0.003341 -7.019559 0.000000

IVa
E= -59.064465
Rb 3.167970 0.000024 0.002860
Rb -2.000850 -0.000098 -0.008292
He -5.018660 2.968401 0.016692
He -5.799095 0.000772 -1.782901
He -5.019465 -2.967718 0.016184
He -5.754503 -0.000085 1.850512

IVb
E= -59.064513
Rb -0.009955 -2.873486 -0.000000
He -0.018968 -7.162122 -0.000000
Rb -0.009955 2.294991 0.000000
He -1.935568 6.039360 0.000000
He 1.161433 5.912455 1.795542
He 1.161433 5.912455 -1.795542

IVc
E= -59.064533
Rb 2.584139 -0.001748 -0.000663
Rb -2.584106 -0.001861 -0.001371
He 6.429672 1.782485 0.008112
He 6.447514 -1.749633 0.008084
He -6.429570 1.783285 0.010513
He -6.448222 -1.749373 0.010937

Va
E= -61.957501
Rb 3.265821 0.000040 0.025875
Rb -1.901836 -0.000131 -0.062937
He -4.571725 3.083631 -1.341302
He -5.012104 1.813245 2.086646
He -5.013722 -1.814713 2.084858
He -6.064721 0.001354 -0.802224
He -4.571448 -3.081826 -1.342325

Vb
E= -61.957555
Rb 2.990203 0.000003 0.000438
He 7.279537 0.000044 0.001562
Rb -2.177633 -0.000052 -0.001640
He -5.953721 -0.000139 1.823582
He -5.198312 -2.967381 0.003704
He -5.962355 0.000214 -1.810532
He -5.197680 2.968153 0.003918

Vc
E= -61.957586
Rb -2.723347 -0.001204 0.003488
Rb 2.444010 0.004637 -0.006490
He 6.111813 -1.550464 -1.371021
He 6.089924 -0.462177 2.046255
He 6.128267 1.955296 -0.605160
He -6.580366 -1.769980 -0.008360
He -6.581908 1.763808 -0.006171

VIa
E= -64.850537
Rb -3.366556 -0.000013 0.000046
Rb 1.801312 0.000025 -0.000262
He 4.583307 -1.165395 2.951010
He 4.583404 2.445717 2.020491
He 4.584892 2.678422 -1.700054
He 4.584709 -0.791050 -3.071387
He 6.036620 -0.001052 0.000150
He 4.584078 -3.166872 -0.196214

VIb
E= -64.850591
Rb -3.089860 0.000133 0.021137
Rb 2.076912 -0.000471 -0.063783
He -7.382607 -0.000439 0.058709
He 5.178018 -1.822530 2.097438
He 4.759561 -3.068640 -1.351464
He 6.252501 0.003893 -0.765249
He 4.755485 3.071633 -1.351167
He 5.176568 1.822342 2.100689

VIc
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Rb -2.326201 -0.000410 0.001148
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He -5.356577 -2.831611 0.866289
He -6.104363 -0.532515 -1.744339
He -5.347828 2.837991 -0.868257
He 6.692363 1.398480 1.108496
He 6.709639 -1.372438 -1.089694

VId
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Rb 2.583591 0.003350 -0.001651
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He 6.243497 -0.140099 2.078012
He 6.242390 -1.745912 -1.136475
He -6.254757 1.791438 -1.029223
He -6.253712 -0.008689 2.070561
He -6.250661 -1.797737 -1.035111

VIIa
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Rb 1.719921 0.000091 0.000126
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He 4.354855 1.297341 -3.134436
He 4.353615 -3.364782 0.443744
He 4.349760 -1.299478 3.139522
He 5.851721 -0.000344 -0.000187
He 4.354866 2.066258 2.690331
He 4.348885 3.369889 -0.444933

VIIb
E= -67.743628
Rb 3.192319 0.000253 0.000167
Rb -1.974566 -0.000467 -0.000684
He -4.763516 -2.150866 -2.331446
He -6.215670 -0.001913 0.000132
He -4.757228 -2.885946 1.327639
He -4.760745 0.371070 3.149464
He -4.763304 1.558846 -2.763478
He -4.756826 3.114399 0.628058
He 7.488852 -0.001631 -0.000794

VIIc
E= -67.743663
Rb -2.941497 -0.000876 0.010060
Rb 2.224353 0.014807 -0.057595
He -6.764950 -1.109552 1.488998
He 5.329265 1.237508 2.489384
He 5.333736 -2.283908 1.579975
He 4.898474 -2.635364 -2.081090
He 4.914903 3.307871 -0.541130
He 6.400786 0.186116 -0.749520
He -6.845058 1.039607 -1.307222

VIId
E= -67.743676
Rb -2.701003 -0.001288 -0.002009
Rb 2.464766 0.001240 0.002109
He 6.243618 -0.003142 -1.828913
He 5.494599 -2.965270 -0.004599
He 6.251594 -0.003752 1.817828
He 5.500250 2.960778 -0.003794
He -6.379050 -1.312477 -1.593896
He -6.371475 2.047397 -0.335301
He -6.369157 -0.722655 1.946824

VIIIa
E= -70.636560
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Rb 3.518325 -0.000192 -0.000116
He -5.593621 1.631760 0.000225
He -4.547156 -0.001142 3.025343
He -3.577233 3.440890 1.984526
He -3.577367 3.441963 -1.982977
He -4.547551 0.000086 -3.025186
He -3.576310 -3.439938 -1.988795
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He -5.590763 -1.640123 0.000052

VIIIb
E= -70.636643
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VIIIc
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VIIId
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He -6.538633 -0.000085 -0.793994
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He -5.483730 1.811971 2.090191
He -5.049929 -3.076557 -1.339528

VIIIe
E= -70.636717
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Rb -2.582533 0.000112 -0.003196
He -5.620114 2.961674 0.112235
He -6.379635 0.063778 -1.802749
He -5.621286 -2.961194 -0.095153
He -6.355536 -0.063969 1.843153
He 6.356390 0.065444 1.842554
He 5.621715 -2.959688 0.112123
He 6.378428 -0.062107 -1.805281
He 5.619382 2.961891 -0.095263

IXa
E= -73.529572
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He -5.490668 -1.768329 0.004260
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He -4.483829 -0.644293 3.027063
He -3.610884 2.589913 2.974834
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He -3.343442 -3.722651 -1.862787
He -3.160883 4.314328 0.017505
Rb -1.585264 -0.031456 -0.000714
Rb 3.581388 -0.002569 0.000086

IXb
E= -73.529650
Rb 1.817503 -0.000911 0.000110
He 4.719284 0.003641 3.026676
He 5.763302 1.639745 0.000519
He 5.766054 -1.629942 0.000036
He 3.754086 -3.442752 -1.978839
He 3.753977 -3.442193 1.979727
He 3.749708 3.442044 -1.986483
He 3.748986 3.442217 1.986694
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He -7.648718 0.004485 0.005960

IXc
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Rb -2.058777 -0.000108 -0.048583
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He -5.340387 -0.038696 2.532827
He -4.195851 -3.391528 1.688196
He -5.994425 -1.631570 -0.612987
He -3.813295 -3.531058 -2.272414

IXd
E= -73.529748
Rb 2.907377 -0.001402 -0.000421
Rb -2.257425 -0.000298 0.000561
He 6.582232 1.974494 -0.648377
He 6.590704 -1.539214 -1.377962
He 6.586071 -0.415894 2.030249
He -5.053384 2.176257 -2.304742
He -5.054288 -1.520663 -2.780135
He -5.057101 -3.111259 0.585597
He -5.056778 -0.401812 3.141919
He -6.508292 0.002523 -0.001096
He -5.053289 2.867008 1.351957

IXe
E= -73.529754
Rb -2.685201 -0.003023 0.008184
Rb 2.479062 0.020870 -0.052780
He 5.168210 3.357787 -0.096868
He -5.754500 2.638000 -1.267052
He 6.656118 0.301571 -0.743317
He 5.170089 -2.352161 -2.393980
He 5.611439 -2.457633 1.257937
He 5.606475 0.907126 2.611686
He -6.461792 0.783778 1.683500
He -5.695917 -2.676735 1.357559
He -6.486538 -0.831898 -1.584435

Xa
E= -76.422577
He 3.717503 1.075330 -3.574278
He 5.354561 -1.085135 -1.646334
Rb 1.523932 -0.035877 -0.000167
He 3.733008 -3.728701 -0.006581
He 5.353813 -1.087872 1.643422
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He 3.714396 1.060487 3.581981
He 3.051835 3.955828 -1.781677
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He 5.194336 1.922895 0.001417
Rb -3.642238 -0.005976 -0.000026
He 3.007115 -2.649346 3.477792
He 3.006852 -2.635202 -3.488432

Xb
E= -76.422663
He -3.503703 -3.748821 1.828242
He -4.656917 -0.641318 3.027448
He -5.660826 -1.775432 0.002395
He -3.511948 -3.728498 -1.857851
He -5.567579 1.594773 0.005253
He -3.771978 2.616794 -2.965415
He -3.340585 4.309148 0.012615
He -3.777506 2.594235 2.978991
He -4.671836 -0.610572 -3.015110
Rb -1.751808 -0.029874 -0.000957
Rb 3.413860 -0.003798 -0.000079
He 7.714919 0.012640 0.002591

Xc
E= -76.422722
Rb 1.960395 0.000656 0.001720
Rb -3.204662 -0.003185 -0.008256
He 3.897940 -3.196554 2.360878
He 3.899764 3.194984 -2.357495
He 3.898050 3.639840 1.594424
He 4.869786 0.337171 3.001446
He 5.911106 -1.626902 0.183908
He 4.875248 -0.333037 -2.995747
He 3.905071 -3.636834 -1.593880
He 5.913135 1.629441 -0.174547
He -7.044412 0.638015 1.707866
He -7.106751 -0.599330 -1.605919

Xd
E= -76.422767
Rb -2.993448 0.000046 0.000590
Rb 2.171071 0.000032 0.000091
He 4.822540 1.904785 -2.802542
He 4.819389 -1.478296 -3.056106
He 4.822581 -3.380539 -0.249430
He 4.820136 -1.906980 2.808546
He 4.826139 1.475803 3.047709
He 4.816085 3.386964 0.246597
He 6.311043 -0.001357 -0.000150
He -6.674918 1.892574 -0.845671
He -6.672800 -1.677900 -1.219394
He -6.676210 -0.216497 2.057845

Xe
E= -76.422788
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He -6.583854 0.000176 -1.818545
Rb -2.789513 -0.000033 -0.000843
He -5.834560 2.964518 0.000574
He -5.834645 -2.964226 -0.000125
Rb 2.374609 0.000094 0.000429
He 5.177207 3.118160 0.565796
He 5.173411 0.424547 3.140937
He 5.176788 -2.855151 1.374740
He 5.178057 -2.189940 -2.291044
He 5.177466 1.501014 -2.791865
He 6.624970 0.000321 0.000839

Xf
E= -76.422789
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Rb -2.581955 0.030818 -0.044437
He -5.314583 -2.086414 -2.579385
He -6.764578 0.406501 -0.661981
He -5.250469 3.371805 0.288243
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He 6.764287 -0.407000 -0.663898
He 5.314505 2.088858 -2.577378
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He 5.250364 -3.371920 0.288029
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