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The Balance of Orbital Overlap and Orbital Energy in the Activation of Methane by Actinide Cations: Insights from Inductively Coupled Plasma Tandem Mass Spectrometry

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Supporting Information

Table S1. Average electronic energy (in eV) of An^+ from the ICP source assuming a Boltzmann distribution.[a]

M^+ (isotope)	Mass (amu)	300 K	700 K	1000 K	6500 K	10000 K
$^{232}Th^+$	232.04	0.00	0.02	0.04	0.77	0.93
$^{231}Pa^+$	231.04	0.00	0.03	0.07	0.35	0.40
$^{238}U^+$	238.05	0.01	0.03	0.05	0.61	0.74
$^{237}Np^+$	237.05	0.00	0.01	0.02	0.26	0.31
$^{242}Pu^+$	242.06	0.00	0.01	0.03	0.80	0.95
$^{243}Am^+$	243.06	0.00	0.00	0.01	0.34	0.75

[a]Masses and electronic states taken from Ref. [1] (https://physics.nist.gov/PhysRefData/Handbook/periodictable.htm)

Table S2. Ionization energies and promotion energies for An^+ and An^{2+}.

M^+	IE(An^+)[a] (eV)	An^+ $E_p(6d7s)$	An^+ $E_p(6d^2)$ (eV)	An^{2+} $E_p(6d)$ (eV)
Th^+	11.9 ± 0.1	0.00	0.00	0.00
Pa^+	11.7 ± 0.5	0.10	0.59	0.00
U^+	11.9 ± 0.5	0.04	0.57	0.026
Np^+	11.7 ± 0.3	0.00	0.9 ± 0.4	0.7 ± 0.4
Pu^+	11.7 ± 0.2	1.08	2.14	1.6 ± 0.4
Am^+	12.0 ± 0.2	1.76	3.6 ± 0.2	3.0 ± 0.4

[a]Compiled and reproduced from Ref. [2]

Table S3. Summary of correlations of the indicated bond dissociation energies with the respective promotion energies.

	r^2 ICP-MS/MS only	r^2 GIBMS Th, U, ICP-MS/MS Pa, Np, Pu, Am
$D_0(AnCD_2^+)$ vs. $E_p(6d^2)$	0.84	0.95
$D_0(AnCD_2^+)$ vs. $E_p(6d7s)$	0.58	0.66
$D_0(AnCD_2^+)$ vs. $IE(An^+) + E_p(6d) - EA(CH_2)$	0.74	0.84
$D_0(AnD^+)$ vs. $E_p(6d)$	0.96	0.91
$D_0(AnCD_3^+)$ vs. $E_p(6d)$	0.97	0.14
$D_0(AnCD^+)$ vs. $E_p(6d^2)$	0.48	0.08

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Statistical mechanics gives
qvib =    1.076D+00 and <Evib> =    7.645D+01 cm-1 (harmonic oscillators)
qrot =    1.429D+05 and <Erot> =    6.082D+02 cm-1 (rigid free rotors)
qhr  =    1.000D+00 and <Ehr>  =    0.000D+00 cm-1 (hindered rotors and electronic states)
qtot =    1.538D+05 (total partition function)

 Energy Population   Energy Population   Energy Population   Energy Population
  0.006  0.024772     0.107  0.054482     0.208  0.011594     0.310  0.001499
  0.019  0.074130     0.120  0.044293     0.221  0.008957     0.322  0.001154
  0.031  0.113397     0.133  0.035236     0.234  0.006928     0.335  0.000894
  0.044  0.120088     0.145  0.030109     0.246  0.005108     0.348  0.000672
  0.057  0.114725     0.158  0.026788     0.259  0.003930     0.360  0.000493
  0.069  0.102734     0.171  0.021955     0.272  0.003082     0.373  0.000375
  0.082  0.087726     0.183  0.018578     0.284  0.002397     0.386  0.000277
  0.095  0.070059     0.196  0.014734     0.297  0.001914     0.398  0.000206

                     Statistical Beyer-Swinehart    Condensed        Truncated
                      Mechanics      T-array       full T-array     32-pt array
Bin size (cm-1):      n/a             3.00          102.00          102.00
Partition Function:   1.53808E+05     1.53273E+05     1.55269E+05     1.54314E+05
Population:           1.00000         0.99653         1.00950         1.00329
Average energy (eV):  0.08488         0.08500         0.08392         0.08431

T(vib) =  350.00 K
BS direct count uses  2669 bins of    3.00 cm-1 up to   8000.00 cm-1
Condensation factor= 34 [Estimated optimum= 33.50]
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Figure S1. Screen capture of the Beyer-Swinehart algorithm output from CRUNCH.[3]

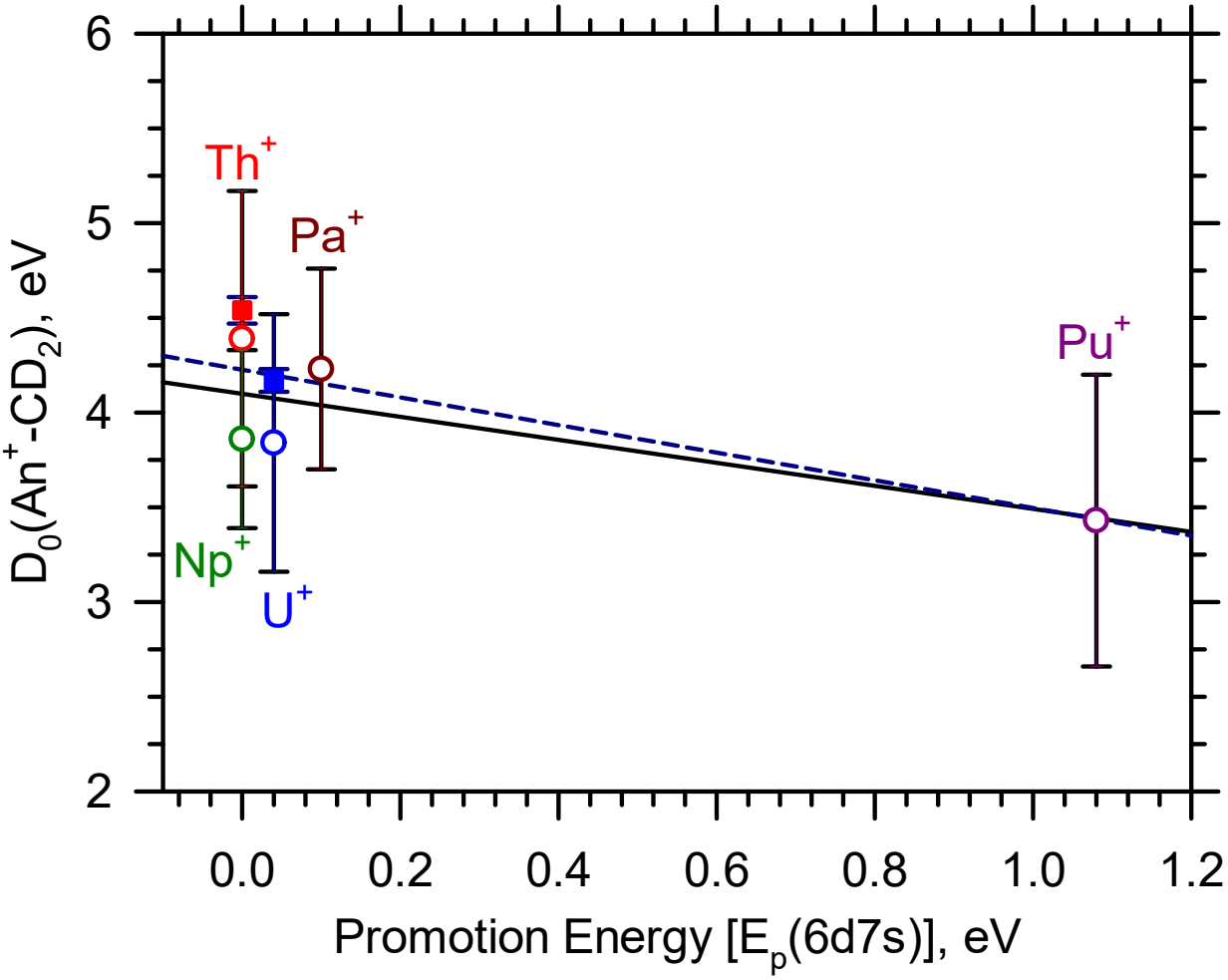

Figure S2. Correlation of $An^+–CD_2$ BDEs with promotion energies of An^+ to a 6d7s electronic configuration. Open circles correspond to BDEs from ICP-MS/MS, and filled squares correspond to BDEs from GIBMS studies of Th[4] and U (unpublished results from Armentrout). The solid black line is the least squares linear regression line using values from ICP-MS/MS ($r^2 = 0.58$), and the dashed blue line is the least squares linear regression line using values from GIBMS for Th and U and values from ICP-MS/MS for Pa, Np, and Pu ($r^2 = 0.66$). Models of the cross section using equation 10 provide threshold energies used to derive $D_0(An^+–CD_2)$.

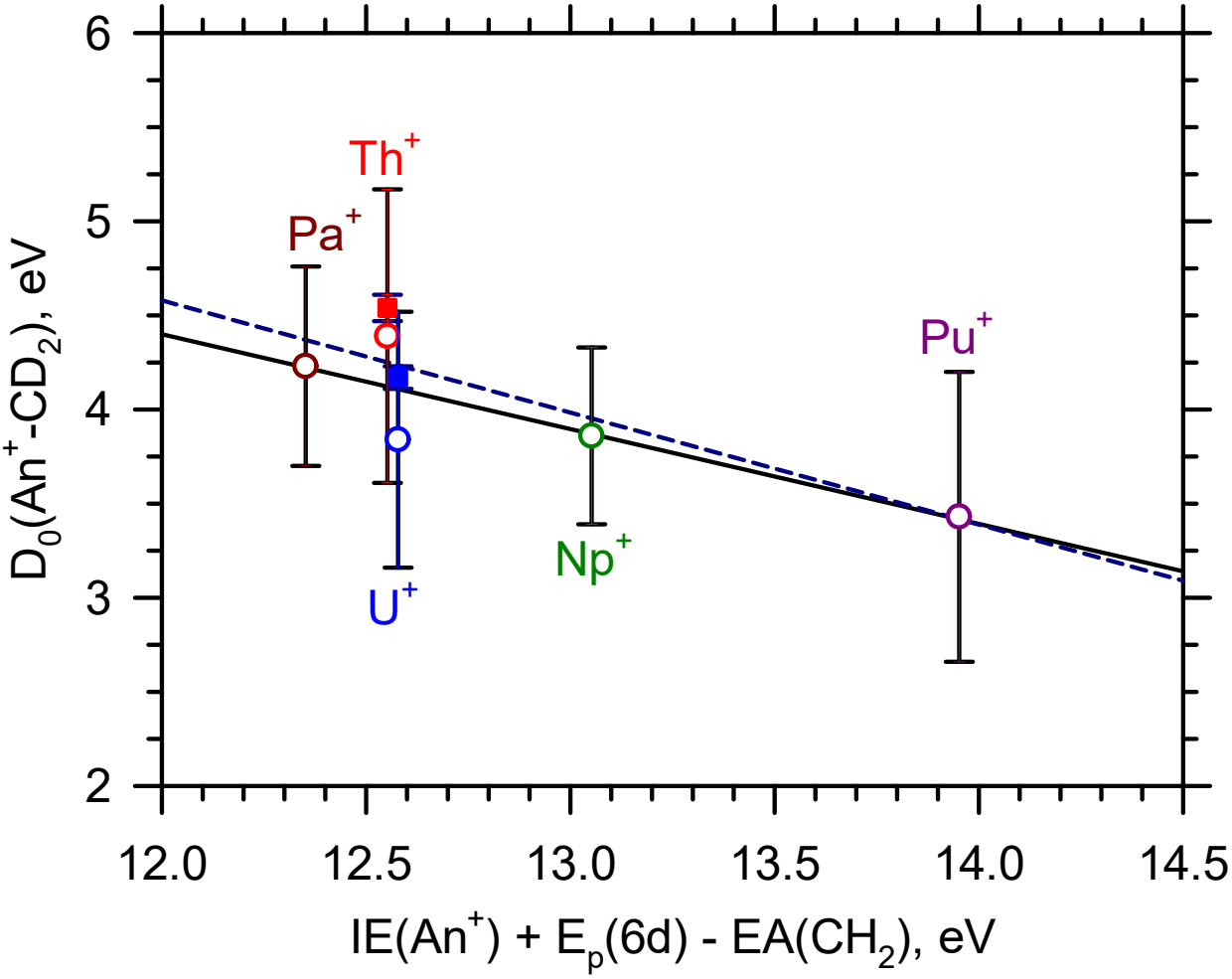

Figure S3. Correlation of $An^+–CD_2$ BDEs from ICP-MS/MS with the sum of the ionization energy of An^+, promotion energy of An^{2+} to a 6d electronic configuration, and the electron affinity of CH_2. Open circles correspond to BDEs from ICP-MS/MS, and filled squares correspond to BDEs from GIBMS studies of Th[4] and U (unpublished results from Armentrout). The solid black line is the least squares linear regression line using values from ICP-MS/MS ($r^2 = 0.74$), and the dashed blue line is the least squares linear regression line using values from GIBMS for Th and U and values from ICP-MS/MS for Pa, Np, and Pu ($r^2 = 0.84$). Models of the cross section using equation 10 provide threshold energies used to derive $D_0(An^+–CD_2)$.

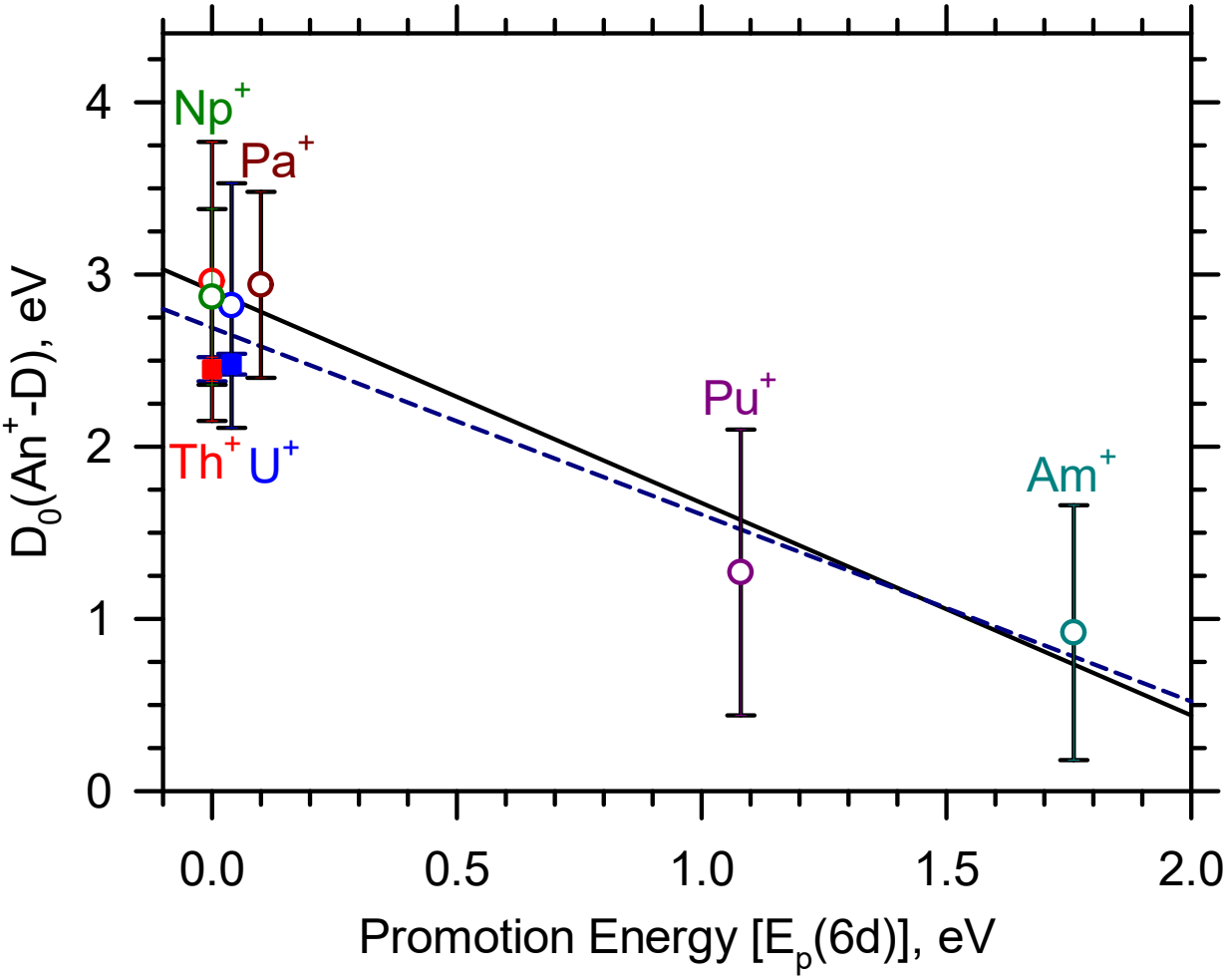

Figure S4. Correlation of An^+−D BDEs with promotion energy of An^+ to a 6d electronic configuration. Open circles correspond to BDEs from ICP-MS/MS, and filled squares correspond to BDEs from GIBMS studies of Th[5] and U[6]. The solid black line is the least squares linear regression line using values from ICP-MS/MS (r^2 = 0.96), and the dashed blue line is the least squares linear regression line using values from GIBMS for Th and U and values from ICP-MS/MS for Pa, Np, Pu, and Am (r^2 = 0.91). Models of the cross section using equation 10 provide threshold energies used to derive $D_0(An^+-D)$.

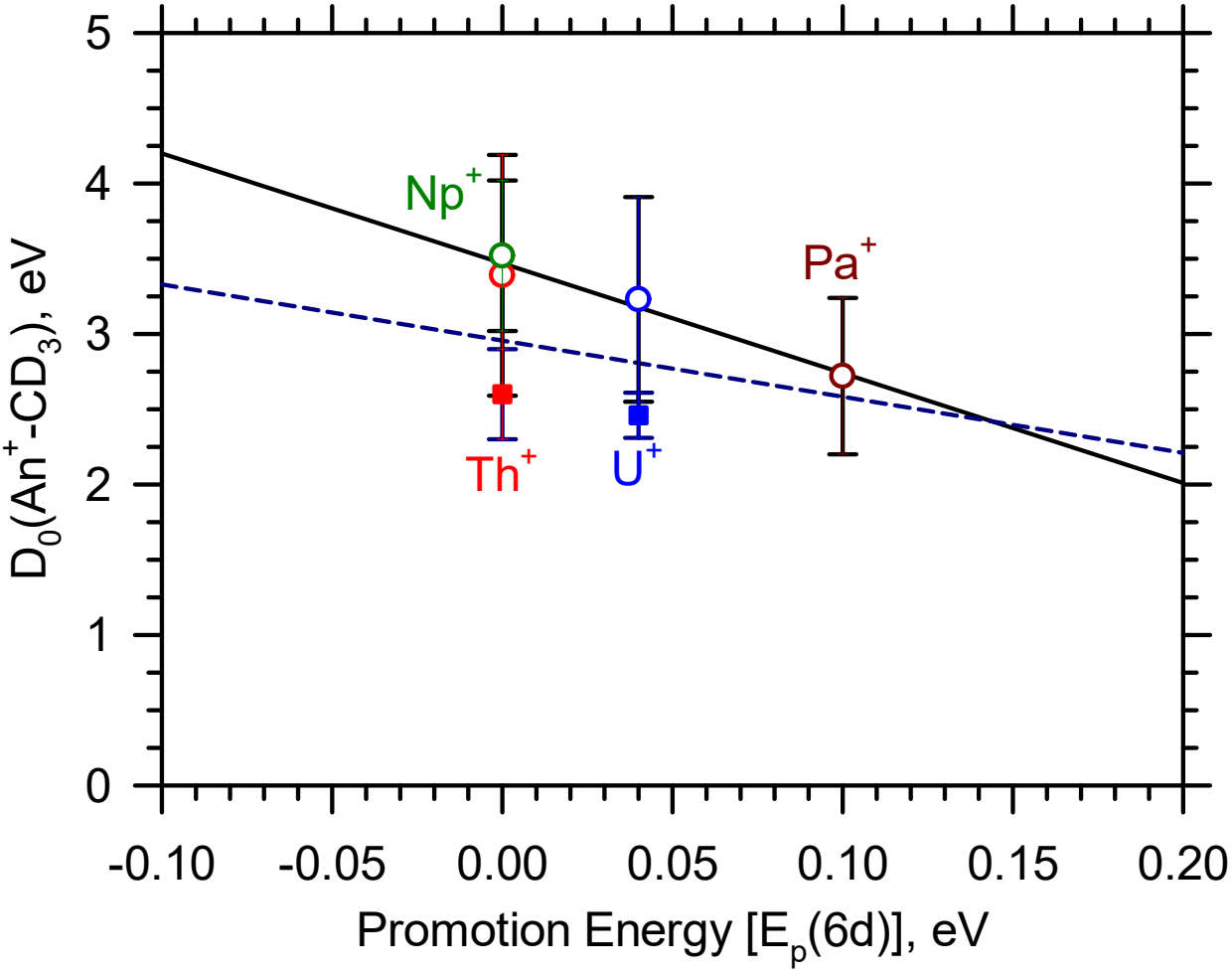

Figure S5. Correlation of $An^+–CD_3$ BDEs with promotion energy of An^+ to a 6d electronic configuration. Open circles correspond to BDEs from ICP-MS/MS, and filled squares correspond to BDEs from GIBMS studies of Th[4] and U (unpublished results from Armentrout). The solid black line is the least squares linear regression line using values from ICP-MS/MS ($r^2 = 0.97$), and the dashed blue line is the least squares linear regression line using values from GIBMS for Th and U and values from ICP-MS/MS for Pa and Np ($r^2 = 0.14$). Models of the cross section using equation 10 provide threshold energies used to derive $D_0(An^+–CD_3)$.

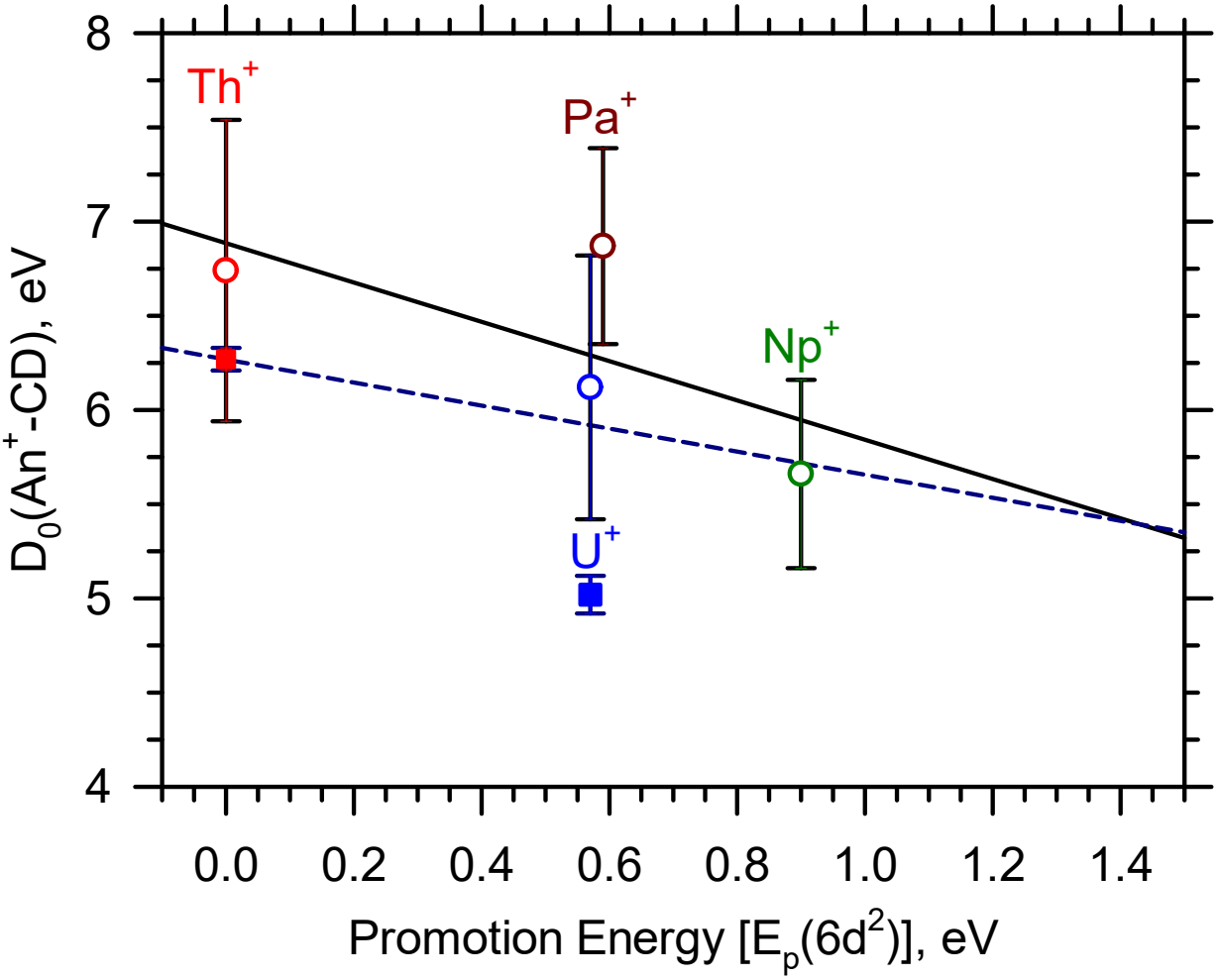

Figure S6. Correlation of An^+−CD BDEs with promotion energy of An^+ to a $6d^2$ electronic configuration. Open circles correspond to BDEs from ICP-MS/MS, and filled squares correspond to BDEs from GIBMS studies of Th[4] and U (unpublished results from Armentrout). The solid black line is the least squares linear regression line using values from ICP-MS/MS ($r^2 = 0.48$), and the dashed blue line is the least squares linear regression line using values from GIBMS for Th and U and values from ICP-MS/MS for Pa and Np ($r^2 = 0.08$). Models of the cross section using equation 10 provide threshold energies used to derive $D_0(An^+-CD)$.

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