Reactions of Laser–ablated U Atoms with $(CN)_2$: Infrared Spectra and Electronic Structure Calculations of UNC, $U(NC)_2$, and $U(NC)_4$ in Solid Argon

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Supporting Material

Experimental methods

The matrix isolation apparatus and procedure for studying laser ablated metal atom reactions has been described previously. The Nd:YAG laser fundamental (Continuum II, 1064 nm, 10Hz repetition rate with 10 ns pulse width) was focused onto a uranium metal target (high purity, depleted of ^{235}U obtained from Oak Ridge National Laboratory) mounted on a rotating rod which produced a bright blue emission plume from the target surface. Laser-ablated uranium species (mostly atoms) were co-deposited with argon or neon (research grade) containing 0.3 to 1% cyanogen gas prepared in this laboratory. We employed thermal decomposition of AgCN at 360-380 deg C until a constant pressure was reached in a stainless steel vacuum line following earlier work. The product gas was condensed at 77 K and evacuated before use. Isotopic reagents were synthesized using $K^{13}CN$ and $KC^{15}N$ (99% enriched, Cambridge Isotopic Laboratories) and silver nitrate to prepare the silver cyanide.

FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 FTIR instrument with a HgCdTe range B detector. Matrix samples were annealed at different temperatures and cooled back to 4 K for spectral recording. Selected samples were subjected to broad band photolysis by a medium-pressure mercury arc street lamp (Philips, 175W) with the outer globe removed using optical glass filters.

References

1. L. Andrews and A. Citra *Chem. Rev.* **2002**, *102*, 885-911.
2. L. Andrews *Chem. Soc. Rev.* **2004**, *33*, 123-132.

Table S1. Relative energies in kcal/mol for $U(NC)_n$ and $U(CN)_n$ compounds predicted with B3LYP functional using the aug-cc-pVTZ basis set on C and N and the ECP60MWB effective core potential and ECP60MWB_SEG basis set on U at 0K.

Molecule	ΔE	Molecule	ΔE	Molecule	ΔE	Molecule	ΔE (0K)
$^{4}UNC(C_{\infty v})$	0.0	$^{5}U(NC)_2\ (C_{2v})$	0.0	$^{4}U(NC)_3\ (C_{3v})$	0.0	$^{3}U(NC)_4\ (S_4)$	0.0
$^{6}UNC(C_{\infty v})$	27.5	$^{5}U(CN)_2\ (C_{2v})$	11.2	$^{4}U(CN)_3\ (C_{3v})$	17.8	$^{1}U(NC)_4\ (C_1)$	28.6
$^{6}UCN(C_{\infty v})$	28.7	$^{3}U(CN)_2\ (C_{2v})$	18.7	$^{2}U(NC)_3\ (C_{3v})$	18.3	$^{3}U(CN)_4\ (C_{2v})$*	30.5
$^{4}UCN(C_{\infty v})$	36.0	$^{3}U(NC)_2\ (C_{2v})$	21.2	$^{2}U(CN)_3\ (C_{3v})$	35.6	$^{1}U(CN)_4\ (D_{2d})$	58.6
$^{2}CUN(C_{\infty v})$	46.4	$^{1}U(NC)_2\ (C_{2v})$	49.2	$^{6}U(NC)_3\ (C_{3v})$	91.7		
		$^{1}U(CN)_2\ (C_{2v})$	64.5	$^{6}U(CN)_3\ (C_{3v})$	119.8		

* Approximate T_d Symmetry

Table S2 Complete frequencies (cm^{-1}) and intensities ($km.mole^{-1}$) for the ground state $U(NC)_n$ and $U(CN)_n$ compounds calculated with B3LYP functional.

$U(NC)_n$	Freq (Inten)	**$U(CN)_n$**	Freq (Inten)
$^{4}UNC\ (C_{\infty v})$	91.9(1), 118.7(0), 389.6(75), 2080.6 (493)	$^{4}UCN(C_{\infty v})$	171.6(0), 219.8(7), 297.3(0), 2072.3 (312)
$^{5}U(NC)_2\ (C_{2v})$	40.5(11), 107.4(0), 112.3(0), 113.8(0), 115.9(0), 365.5(151), 383.7(35), 2072.3(681), 2084.0(171)	$^{5}U(CN)_2\ (C_{2v})$	38.6(12), 117.3(0), 128.6(0), 136.2(0), 187.2(0), 320.2 (99), 330.0(22), 2213.3(67), 2214.8(15)
$^{4}U(NC)_3\ (C_{3v})$	38.8(25), 42.7(6), 47.4(7), 51.4(3), 93.8(0), 127.7(1), 131.3(1), 144.1(1), 215.1(13), 379.0(159), 382.7(159), 395.5(26), 2072e (1453), 2088.7 (54)	$^{4}U(CN)_3\ (C_{3v})$	41.0(26), 47.7(9), 49.1(9), 117.5(3), 121.8(2), 133.5(0), 158.8(0), 182.9(1), 184.5(1), 343.3e(210), 350.1(17), 2219e (195), 2220.7 (17)
$^{3}U(NC)_4\ (S_4)$	46.2(0), 46.4(1), 47.5(14), 48.8e(24), 98.0(0), 102.3(0), 102.4(0), 118.1e(2), 135.6(0), 142.9(2), 158.8(0), 404.6e(414), 405.1(173), 426.7(0), 2045.6(927), 2045.6 (927), 2046.4e (2100) , 2086 (0)	$^{3}U(CN)_4\ (C_{2v})$*	42.1(7), 43.2(8), 45.1(13), 47.0(12), 49.3(6) 130.6(0), 136.2(0), 138.4(0), 167.4(1), 170.7(0), 174.4(0), 191.1(0), 233.0(0), 361.5(43), 364.2 (79), 364.6 (125), 364.9(121), 2220.0 (215), 2220.1 (210), 2220.8 (217), 2227.1 (2)

* Approximate T_d Symmetry

Table S3. NBO6 Population Analysis with the B3LYP Functional for the lowest energy states of $U(NC)_n$ for n = 1 to 4

Molecule	Spin, electron config	7s total pop spin (α, β)	5f total pop spin(α, β)	6d total pop spin (α, β)	7p total pop spin (α, β)
^{4}UNC	3 (f^3)	1.87 (0.93, 0.94)	3.05 (3.02, 0.03)	0.26 (0.14, 0.12)	0.01 (0.01,0.01)
^{6}UNC	5 ($s^1d^1f^3$)	0.94 (0.90, 0.03)	3.16 (3.14, 0.02)	1.06 (1.01, 0.05)	0.01 (0.01, 0)
$^5U(NC)_2$ (C_{2v})	4 (s^1f^3)	0.83 (0.77, 0.06)	3.07 (3.02, 0.05)	0.54 (0.41, 0.14)	0.01 (0.01,0)
$^4U(NC)_3$ (C_{3v})	3 (f^3)	0.14 (0.09, 0.06)	3.08 (2.98, 0.10)	0.54 (0.30, 0.25)	0.01 (0,0)
$^3U(NC)_4$ (S_4)	2 (f^2)	0.14 (0.07, 0.07)	2.42 (2.17, 0.25)	0.95 (0.49, 0.46)	0.01 (0.01,0.01)
^{4}UCN	3 (f^3)	0.94 (0.87, 0.07)	3.00 (2.97, 0.03)	1.22 (0.32, 0.90)	0.02 (0.01,0.01)
^{6}UCN	5 ($s^1d^1f^3$)	0.98 (0.92, 0.07)	3.48 (3.46, 0.02)	0.70 (0.64, 0.05)	0.02 (0.02, 0)
$^5U(CN)_2$ (C_{2v})	4 (s^1f^3)	0.87 (0.76, 0.11)	3.06 (3.02, 0.04)	0.65 (0.48, 0.16)	0.01 (0.01,0)
$^4U(CN)_3$ (C_{3V})	3 (f^3)	0.30 (0.16, 0.13)	3.06 (2.99, 0.07)	0.67 (0.36, 0.31)	0 (0,0)
$^3U(CN)_4$ (C_{2v})*	2 (f^2)	0.34 (0.17, 0.17)	2.39 (2.17, 0.22)	1.22 (0.63, 0.59)	0.01 (0.01,0.01)

* Approximate T_d Symmetry. Charges on C and N averaged.

Table S4. B3LYP Bond Distances (Å) in $U(NC)_n$ and $U(NC)_n$

isocyano	r(NC)	r(UN)	cyano	r(NC)	r(UC)
^{4}UNC	1.180	2.258	^{4}UCN	1.169	2.376
^{6}UNC	1.177	2.349	^{6}UCN	1.164	2.452
$^5U(NC)_2$ (C_{2v})	1.179	2.277	$^5U(CN)_2$ (C_{2v})	1.161	2.429
$^4U(NC)_3$ (C_{3v})	1.180	2.283	$^4U(CN)_3$ (C_{3V})	1.160	2.423
$^3U(NC)_4$ (S_4)	1.183	2.235	$^3U(CN)_4$ (C_{2v})*	1.160	2.365

* Approximate T_d Symmetry. Bond distances averaged.

Table S5. NPA Charges for $U(NC)_n$ and $U(NC)_n$

isocyano	U	N	C	NC	Cyano	U	C	N	CN
^4UNC	0.830	-1.109	0.279	-0.83	^4UCN	0.843	-0.441	-0.401	-0.84
^6UNC	0.847	-1.059	0.211	-0.85	^6UCN	0.838	-0.422	-0.416	-0.84
$^5U(NC)_2$ (C_{2v})	1.579	-1.063	0.273	-0.80	$^5U(CN)_2$ (C_{2v})	1.449	-0.381	-0.344	-0.72
$^4U(NC)_3$ (C_{3V})	2.277	-1.044	0.285	-0.76	$^4U(CN)_3$ (C_{3V})	2.031	-0.360	-0.316	-0.68
$^3U(NC)_4$ (S_4)	2.530	-1.000	0.368	-0.63	$^3U(CN)_4$ (C_{2v})*	2.125	-0.296	-0.234	-0.53

* Approximate T_d Symmetry. Charges on C and N averaged.

Table S6. Total energies at 0K with the B3LYP functional (E_{total}, a.u.) and geometries (x, y, z Cartesian coordinates in Å) for the lowest energy states of $U(NC)_n$ and $U(CN)_n$ for n = 1 to 4.

$U(NC)_n$

^{4}UNC C_{infv} E_{total} =-569.770847

U	0.000000	0.000000	0.346983
C	0.000000	0.000000	-3.091003
N	0.000000	0.000000	-1.910921

^{6}UNC C_{infv} E_{total} =-569.727076

U	0.000000	0.000000	0.358116
C	0.000000	0.000000	-3.168001
N	0.000000	0.000000	-1.991244

$^5U(NC)_2$ C_{2v} E_{total} =-662.69046

U	0.000000	0.000000	0.307641
N	0.000000	1.957177	-0.867835
N	0.000000	-1.957177	-0.867835
C	0.000000	3.035092	-1.346107
C	0.000000	-3.035092	-1.346107

$^3U(NC)_2$ C_{2v} E_{total} =-662.656622

U	0.000000	0.000000	0.321793
N	0.000000	1.832676	-0.940126
N	0.000000	-1.832676	-0.940126
C	0.000000	2.932473	-1.370270
C	0.000000	-2.932473	-1.370270

$^4U(NC)_3$ C_{3v} E_{total} =-755.614049

U	-0.000268	-0.000037	-0.250036
C	2.746799	-1.864842	0.679024
C	-2.988208	-1.445147	0.676042
C	0.246813	3.309652	0.674267
N	-1.939008	-0.930266	0.517126
N	1.778421	-1.212734	0.511351
N	0.159477	2.143773	0.518280

$^2U(NC)_3$ C_{3v} E_{total} =-755.584955

U	-0.000722	-0.002219	-0.007759
N	-0.002074	2.291654	0.037749
N	-1.983990	-1.162995	-0.012001
N	2.004678	-1.128849	0.014540
C	-0.039918	3.470489	0.004976
C	-3.010569	-1.741688	0.043838
C	3.039848	-1.694560	0.023158

$^{3}U(NC)_4$ S_4 E_{total} =-848.495965

U	0.000074	0.000171	0.000220
N	0.169861	-1.884757	-1.188458
N	1.888144	0.169211	1.184101
N	-0.171795	1.888292	-1.183087
N	-1.885537	-0.172973	1.187421
C	2.867070	0.255816	1.843335
C	0.256758	-2.861075	-1.851511
C	-0.262809	2.865941	-1.843620
C	-2.862937	-0.263044	1.848452

$^{1}U(NC)_4$ C_1 E_{total} =-848.450417

U	-0.000891	-0.001541	-0.028570
N	0.276242	1.952910	0.985846
N	1.884512	-0.424653	-1.164535
N	-0.222995	-1.561979	1.532799
N	-1.934345	0.030489	-1.167691
C	2.823241	-0.671099	-1.841847
C	0.431875	2.985351	1.543239
C	-0.352926	-2.379407	2.378770
C	-2.892508	0.092552	-1.859580

$U(CN)_n$

^{4}UCN C_{infv} E_{total} =-569.713414

C	0.000000	0.000000	-2.003688
U	0.000000	0.000000	0.372050
N	0.000000	0.000000	-3.172357

^{6}UCN C_{infv} E_{total} =-569.725051

C	0.000000	0.000000	-2.070949
U	0.000000	0.000000	0.381161
N	0.000000	0.000000	-3.234450

$^{5}U(CN)_2$ C_{2v} E_{total} =-662.672669

U	0.000000	0.000000	0.325263
C	0.000000	2.102932	-0.889764
C	0.000000	-2.102932	-0.889764
N	0.000000	3.157312	-1.374787
N	0.000000	-3.157312	-1.374787

$^{3}U(CN)_2$ C_{2v} E_{total} =-662.660627

U	0.000000	0.000000	0.317649
C	0.000000	2.119896	-0.871357
C	0.000000	-2.119896	-0.871357
N	0.000000	3.181401	-1.340533
N	0.000000	-3.181401	-1.340533

$^{4}U(CN)_3$ C_{3v} E_{total} =-755.585749

U	0.265052	0.093559	0.000000
C	-0.146701	-1.258650	1.967705
C	-1.278755	1.961251	0.000000
C	-0.146701	-1.258650	-1.967705
N	-0.146701	-1.864092	-2.957414
N	-0.146701	-1.864092	2.957414
N	-1.842583	2.975169	0.000000

$^{2}U(CN)_3$ C_{3v} E_{total} =-755.557286

U	0.258888	0.104118	0.000000
C	-0.100047	-1.272163	1.952654
C	-1.333013	1.917114	0.000000

C	-0.100047	-1.272163	-1.952654
N	-0.100047	-1.883407	-2.938931
N	-0.100047	-1.883407	2.938931
N	-1.888340	2.936018	0.000000

$^{3}U(CN)_4$ T_d E_{total} =-848.447318

U	0.002105	-0.000093	-0.009692
C	-0.160410	-1.893105	1.393465
C	2.027990	-0.113242	-1.225019
C	0.014437	1.952121	1.320033
C	-1.893076	0.054641	-1.423135
N	-0.237424	-2.824842	2.080408
N	3.006483	-0.168003	-1.845965
N	0.022099	2.912247	1.971225
N	-2.809343	0.081471	-2.134290

$^{1}U(CN)_4$ C_{2v} E_{total} =-848.402612

U	0.000000	0.000000	0.000816
C	0.000000	1.939323	1.340015
C	1.938243	0.000000	-1.340426
C	-1.938243	0.000000	-1.340426
C	0.000000	-1.939323	1.340015
N	2.897728	0.000000	-1.993403
N	0.000000	2.901959	1.988391
N	-2.897728	0.000000	-1.993403
N	0.000000	-2.901959	1.988391