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Infrared Spectra and Quantum Chemical Calculations of the Uranium Carbide Molecules UC and CUC with Triple Bonds

Xuefeng Wang,[†] Lester Andrews,*,[†] Per-Åke Malmqvist,[‡] Björn O. Roos,[‡] António P. Gonçalves,[§] Cláudia C. L. Pereira,[§] Joaquim Marçalo,[§] Claude Godart,[||] and Benjamin Villeroy[||]

Department of Chemistry, University of Virginia, Charlottesville, Virginia, 22904-4319, Department of Theoretical Chemistry, Chemical Center, University of Lund, POB 124, 2-221 00 Lund, Sweden, Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear/CFMCUL, 2686-953 Sacavém, Portugal, and Chimie Métallurgique des Terres Rares, ICMPE, CNRS, 2/8 rue Henri Dunant, 94320 Thiais, France

Received March 31, 2010; E-mail: lsa@virginia.edu

Abstract: Laser evaporation of carbon-rich uranium/carbon alloys followed by atom reactions in a solid argon matrix and trapping at 8 K gives weak infrared absorptions for CUO at 852 and 804 cm^{-1}. A new band at 827 cm^{-1} becomes a doublet with mixed carbon 12 and 13 isotopes and exhibits the 1.0381 isotopic frequency ratio, which is appropriate for the UC diatomic molecule, and another new band at 891 cm^{-1} gives a three-band mixed isotopic spectrum with the 1.0366 isotopic frequency ratio, which is characteristic of the linear CUC molecule. CASPT2 calculations with dynamical correlation find the C≡U≡C ground state as linear $^3\Sigma_u^+$ with 1.840 Å bond length and molecular orbital occupancies for an effective bond order of 2.83. Similar calculations with spin-orbit coupling show that the U≡C diatomic molecule has a quintet ($\Lambda = 5$, $\Omega = 3$) ground state, a similar 1.855 Å bond length, and a fully developed triple bond of 2.82 effective bond order.

Introduction

Uranium carbides are hard, refractory ceramic materials which exist in several stoichiometries including uranium monocarbide, UC, diuranium tricarbide, U_2C_3, and uranium dicarbide, UC_2.[1,2] Uranium dicarbide is used as a fuel for nuclear reactors, usually in the form of solid pellets either as the carbide or mixed with the dioxide. Such fuel is proposed in designs for nuclear-powered rockets owing to better power density. Thus, uranium carbides are appropriate as fuels for new generations of nuclear reactors.[3-5]

Solid uranium carbides are very stable, and small molecules containing uranium and carbon will also be stable and probably contain multiple bonds if methods can be devised to prepare and investigate these molecules. Mass spectroscopic evidence has been obtained for UC_2 as a trace component in the vapor over solid UC_2 at 2400−2700 K and for UC from the pressure-independent equilibrium $UC_2(g) + U(g) = 2UC(g)$ over a uranium−boron alloy plus carbon at 2500−2800 K.[6] Subsequent mass spectroscopic measurements of atomization energies suggest that polyatomic uranium carbides will contribute to the vapor phase of the uranium−carbon system over 3000 K.[7]

The reaction of laser-ablated U atoms and CO molecules produced the stable CUO molecule, which is isoelectronic with the ubiquitous UO_2^{2+} uranyl dication.[8-10] Unfortunately, this approach cannot be applied to binary uranium carbides such as CUC since clean sources of molecular C_2 as a reagent, particularly with the carbon-13 isotopic enrichment necessary for vibrational analysis, are not readily available. Hence, we must find a new method to produce U and C atoms for reaction under conditions where novel molecular products can be isolated, and laser evaporation of arc melted uranium/carbon alloy targets, which can be prepared with carbon-13 using a newly developed technique, appeared to be promising. Accordingly, U/C alloy targets were laser evaporated at temperatures in excess of 3300 K, and the resulting atoms were reacted in a solid argon matrix environment and trapped at 8 K.

† University of Virginia.
‡ University of Lund.
§ Instituto Tecnológico e Nuclear/CFMCU.
|| ICMPE.

(1) (a) Austin, A. E. *Acta Crystallogr.* **1959**, *12*, 159–161. (b) Bowman, A. L.; Arnold, G. P.; Witteman, W. G.; Wallace, T. C.; Nereson, N. G. *Acta Crystallogr.* **1966**, *21*, 670–671.
(2) (a) Atoji, M. *J. Chem. Phys.* **1967**, *47*, 1188–1189. (b) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, UK, 1984.
(3) Hunt, R. D.; Lindemer, T. B.; Hu, M. Z.; Del Cul, G. D.; Collins, J. L. *Radiochim. Acta* **2007**, *94*, 225–232.
(4) Utton, C. A.; De Bruycker, F.; Boboridis, K.; Jardin, R.; Noel, H.; Gueneau, C.; Manara, D. *J. Nucl. Mater.* **2009**, *385*, 443–448.
(5) (a) Vasudevamurthy, G.; Knight, T. W. *Nuclear Tech.* **2008**, *163*, 321–327. (b) Petti, D.; Crawford, D.; Chauvin, N. *MRS Bull.* **2009**, *34*, 40–45.

(6) (a) Norman, J. H.; Winchell, P. *J. Phys. Chem.* **1964**, *68*, 3802–3805, and references therein. (b) Gingerich, K. A *J. Chem. Phys.* **1969**, *50*, 2255–2256.
(7) Gupta, S. K.; Gingerich, K. A. *J. Chem. Phys.* **1979**, *71*, 3072–3080.
(8) Zhou, M. F.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 9712–9721.
(9) Li, J.; Bursten, B. E.; Liang, B.; Andrews, L. *Science* **2002**, *295*, 2242–2245.
(10) Andrews, L.; Liang, B.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **2003**, *125*, 3126–3139.

Multiple bonding between uranium and main group elements has become of considerable interest.[11-17] Uranium forms numerous U=O bonds, but fewer U=NX and U=CX$_2$ bonds are known. The imido (An=NX), phosphinidene (An=PX), and N−U−N molecular linkages have been prepared,[13-17] and the simple NH=UH$_2$, CH$_2$=UH$_2$, CH$_2$=UHX, CH$_2$=UX$_2$, and CH≡UX$_3$ molecules have been produced and identified in matrix isolation experiments and characterized by density functional theory calculations.[18-22] Ligand-supported uranium carbene complexes have been prepared, and the uranium−carbon bond has been measured in uranium phosphoylide and nucleophilic carbene complexes, but the bond lengths are much longer than computed for the above simple methylidene complexes.[23,24] Hence, the preparation and characterization of isolated binary uranium carbon bearing molecules containing multiple bonds is of practical and fundamental importance.

Experimental Details

The material evaporated from arc-melted, depleted uranium/carbon alloy targets using a pulsed YAG laser, as described previously for pure metals,[25] was collected in a condensing argon stream at 6−8 K. A standard arc furnace melting method was employed for reacting cleaned uranium turnings and graphite pieces,[26] and alloy targets with U/C mole ratios of 1/2, 1/4, and 1/7 were used to produce new infrared absorptions. Powder X-ray patterns showed that these targets are mixtures of UC$_2$ and graphite. Unfortunately, this method did not work for amorphous carbon-13 powder, which is the only available form of pure solid carbon-13 isotopic material.[27] However, the spark plasma sintering technique employed for ceramics[28] was adapted to make a dense pellet of solid carbon-13 from amorphous carbon-13 powder. This carbon-13 pellet was then arc melted with normal isotopic graphite and cleaned uranium turnings to form the U/C-12/C-13 and U/C-13 pellets employed here (U/C mole ratios 1/4).
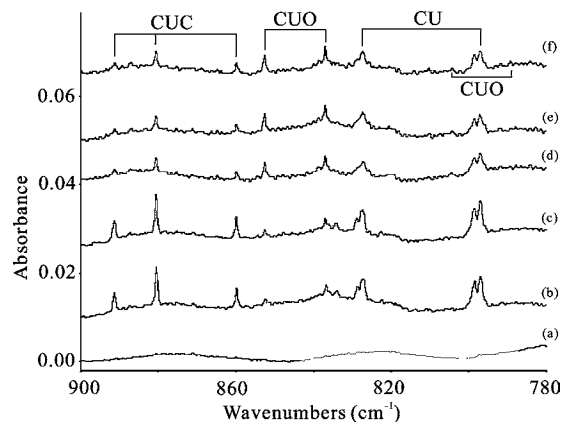
(11) Burns, C. J. *Science* **2005**, *309*, 1823–1824.
(12) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941–1943.
(13) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835–1838.
(14) Gagliardi, L.; Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 1573–1576.
(15) Ephritikhine, M. *Dalton Trans.* **2006**, 2501–2516.
(16) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514–516.
(17) Arney, D. S.; Burns, C. J.; Schnabel, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 6780–6781.
(18) Wang, X.; Andrews, L.; Marsden, C. J. *Chem.—Eur. J.* **2005**, *14*, 9192–9201 (NH=UH$_2$).
(19) (a) Lyon, J. T.; Andrews, L.; Malmqvist, P.-Å.; Roos, B. O.; Yang, T.; Bursten, B. E *Inorg. Chem.* **2007**, *46*, 4917–4925. (b) Roos, B. O.; Lindh, R.; Cho, H.-G.; Andrews, L. *J. Phys. Chem A* **2007**, *111*, 6420–6424 (CH$_2$=UH$_2$).
(20) Lyon, J. T.; Andrews, L. *Inorg. Chem.* **2006**, *45*, 1847–1852 (CH$_2$=UHX).
(21) Lyon, J. T.; Andrews, L.; Hu, H.-S.; Li, J. *Inorg. Chem.* **2008**, *47*, 1435–1442 (CH$_2$=UF$_2$).
(22) Lyon, J. T.; Hu, H.-S.; Andrews, L.; Li, J. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 18919–18924 (CH≡UX$_3$). CH≡UF$_3$ has a 2.56 effective UC bond order.
(23) (a) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589. (b) Stevens, R. C.; Bau, R.; Cramer, R. E.; Afzal, D.; Gilje, J. W.; Koetzle, T. F. *Organometallics* **1990**, *9*, 694.
(24) Cantat, T.; Arliguie, T.; Noel, A.; Thuery, P.; Ephritikhine, M.; Le Floch, P.; Mezailles, N. *J. Am. Chem. Soc.* **2009**, *131*, 963–972.
(25) Andrews, L.; Cho, H.-G. *Organometallics* **2006**, *25*, 4040–4053 (review article).
(26) Kruger, O. L.; Armstrong, J. L. *Rev. Sci. Instrum.* **1964**, *35*, 156 (arc furnace).
(27) Cambridge Isotope Laboratories, Cambridge, MA, www.isotope.com.
(28) Omori, M.; Hirai, T. *New Ceram.* **1994**, *7*, 23 (spark plasma sintering).

Figure 1. Infrared spectra of uranium and carbon atom reaction products in the 900−780 cm^{-1} region: (a) U and C from laser evaporation of alloy target [U/C = 1/4, ^{12}C/^{13}C = 1/1] codeposited in excess argon at 8 K for 60 min, (b) after annealing to 20 K, (c) after annealing to 30 K, (d) after >290 nm irradiation for 20 min, (e) after annealing to 30 K, and (f) after annealing to 35 K.

Although spark plasma sintering is commonly used to produce dense metals, intermetallics, and ceramics, there are no reports on the application of this technique to produce dense solids from amorphous starting powders. This new treatment of solid carbon-13 will find other applications that require stable isotopic substitution in spectroscopy, intermetallics, and ceramics.

Results and Discussion

Infrared spectra of the reaction products formed from ablated material were recorded, and the freshly deposited sample reveals very weak bands that increase on annealing to 20 and 30 K. Weak C$_3$, C$_2$O, and UO bands[29-31] are observed at 2039.2, 1968.9, and 820.0 cm^{-1}, and a moderate CO absorption appears at 2138.5 cm^{-1} in these experiments. Weak bands at 852.6 and 804.4 cm^{-1} are in agreement with absorptions reported for the triplet state CUO molecule isolated in and interacting with argon.[9,10] Significant new reaction product bands appeared at 891.4 and 827.4 cm^{-1}, and the C$_3$ band also increased on annealing. Ablation of a U/C-13 pellet produced these new bands shifted to 859.9 and 797.0 cm^{-1} with ^{13}C$_3$ at 1960.9 cm^{-1}, and ^{13}C$_2$O at 1918.4 cm^{-1}.

The most important experiments were performed using the target containing uranium with half carbon-12 and half carbon-13, which is necessary to determine the carbon stoichiometry of the new product molecules from vibrational spectroscopy. These spectra, shown in Figure 1 after sample deposition, annealing, and >290 nm irradiation, contained carbon isotopic doublets for the first bands at 852.6, 837.0 cm^{-1} and at 804.3, 789.1 cm^{-1} for the CUO molecule containing a single carbon atom.[9,10] An isotopic doublet was observed at 827.4 and 797.0 cm^{-1} for the lower new product and a triplet at 891.4, 880.6, and 859.9 cm^{-1} for the higher new band. An isotopic doublet was also observed at 2138.5 and 2091.4 cm^{-1} for ^{12}CO and ^{13}CO, respectively, with absorbances of 0.024 and 0.018. These CUO products are probably made here first on annealing by reaction of UO evaporated from the alloy target surface with C atoms in the matrix and on >290 nm photolysis as observed

(29) Weltner, W., Jr; McLeod, D., Jr. *J. Chem. Phys.* **1964**, *40*, 1305.
(30) (a) Jacox, M.; Milligan, D. E.; Moll, N. G.; Thompson, W. E. *J. Chem. Phys.* **1965**, *43*, 3734. (b) DeKock, R. L.; Weltner, W., Jr; McLeod, D., Jr. *J. Chem. Phys.* **1971**, *93*, 7106.
(31) Hunt, R. D.; Andrews, L. *J. Chem. Phys.* **1993**, *98*, 3690 (UO, UO$_2$ and UO$_3$).

Table 1. Calculated Structural Parameters and Harmonic Frequencies for UC and CUC[a]

molecule	CASPT2	B3LYP	BPW91	obsd in Ar
UC	1.855[b]	1.859	1.864	
^{5}X	938	934 (116)	908 (100)	827.4
CUC	1.840/180[b]	1.834/180	1.846/180	
$^3\Sigma_u^+$	933 (σ_u)[c]	976 (σ_u, 252)	952 (σ_u, 228)	891.4
	889 (σ_g, 0)	918 (σ_g, 0)	891 (σ_g, 0)	
		110 (π_u, 88 × 2)	54 (π_u, 89 × 2)	

[a] Calculations performed at the CASPT2//ANO-RCC-VTZP, B3LYP, or BPW91//6-311+G(3df)//SDD level. [b] Bond lengths/angles are in Å and deg. [c] Frequencies in cm^{-1} with mode symmetry, intensities, km/mol, in parentheses. CASPT2 values are corrected for anharmonicity.

before from the U + CO reaction.[8−10] The C_3 absorption doubled on the annealing sequence, which also attests to the diffusion and reaction of C atoms in these samples. The observation of a known single U atom bearing species, CUO, suggests strongly that these new product molecules also most likely contain single U atoms, a fact substantiated by the carbon isotopic vibrational analysis below. Finally, the C_3 absorption produced a mixed carbon isotopic sextet, which confirms randomization of the carbon atoms in these samples.[29]

First, the new carbon isotopic doublet at 827.4 and 797.0 cm^{-1} is due to another single carbon atom bearing species, and it exhibits the carbon-12/carbon-13 isotopic frequency ratio 1.0381. This is near and slightly lower than the 1.0388 value calculated for a harmonic U−C diatomic oscillator, which is appropriate for the UC diatomic molecule with a small anharmonic contribution to the vibrational potential function. Quantum chemical calculations using the hybrid B3LYP and pure BPW91 density functionals as performed previously[25,32−34] find a quintet ground state for UC with 1.859 and 1.864 Å bond lengths and 934 and 908 cm^{-1} harmonic vibrational frequencies, respectively (Table 1). The wave function based CASPT2 method with spin orbit coupling[35−37] results in the quintet ground state ($\Lambda = 5$, $\Omega = 3$) for UC with the 1.855 Å bond length and a 945 cm^{-1} harmonic or 938 cm^{-1} anharmonic frequency. The calculation of vibrational frequencies is not an exact science, but the close agreement of two different density functional and state of the art wave function frequency calculations points to a higher frequency for UC than the 827 cm^{-1} argon matrix observation. Subsequent neon matrix experiments find this carbon isotopic doublet blue-shifted to 871.6 and 839.6 cm^{-1}, which is more in line with the results of calculations that still slightly overestimate the observed frequency.[38,39] The neon

matrix value is higher and nearer to the computed values, which is the typical matrix host relationship where argon interacts more strongly with the guest molecule.[40] Since the 44 cm^{-1} argon to neon matrix shift is larger than normal, it is possible that a different electronic state of UC is trapped in solid argon than in solid neon, which will be investigated through further calculations. It is difficult to predict the gas phase UC ground state fundamental frequency from these observations, but 900 ± 10 cm^{-1} is reasonable. Finally these calculations substantiate this preparation and identification of the UC diatomic molecule.

Next, the new isotopic triplet with 1/2/1 relative intensity components is clearly due to a new molecule with two equivalent carbon atoms as double-statistical weight applies to the two equivalent 12−13 and 13−12 orientations. Furthermore, a linear CUC molecule would have an antisymmetric U−C stretching mode with a harmonic carbon-12/carbon-13 isotopic frequency ratio of 1.0370, which is slightly higher than the observed 1.0366 value owing to anharmonicity in the observed frequencies. Thus, the mixed carbon isotopic triplet and the magnitude of the carbon-13 shift for the 891.4 cm^{-1} absorption clearly identify the linear CUC molecule.

Preliminary density functional calculations using the BPW91 functional predict a linear CUC molecule in the $^3\Sigma_u^+$ ground state with intense antisymmetric harmonic stretching frequency at 952.0 cm^{-1} (228 km/mol intensity), ^{12}CU^{13}C component at 939.5 cm^{-1} (208 km/mol) with symmetric counterpart at 868.8 cm^{-1} (12 km/mol), and ^{13}CU^{13}C counterpart at 918.0 cm^{-1} (212 km/mol). The observed isotopic ratios 891.4/880.6 = 1.0123 and 891.4/859.9 = 1.0366 are slightly lower than the calculated ratios (1.0133 and 1.0370) for the reason discussed above. Furthermore, the asymmetry in the carbon isotopic triplet is due to the unobserved symmetric stretching mode falling at lower frequency (calculated for ^{12}CU^{12}C at 890.9 cm^{-1}) and interacting with the antisymmetric mode in the mixed ^{12}CU^{13}C isotopic molecule of lower symmetry. As a result, the computed intensity of the central component is reduced by 12 km/mol, which appears in the symmetric mode counterpart given above. The observed carbon isotopic multiplet absorbances also reveal this behavior: 891.4 cm^{-1} (0.0044 absorbance, ± 0.0001), 880.6 cm^{-1} (0.0083 a), and 859.9 cm^{-1} (0.0045 a). Although there is a small isotopic effect on intensity, the carbon-12 and -13 in these samples are approximately equally abundant, and the central mixed isotopic component should in the absence of any interaction be stronger, about 0.0089 a. It is observed to be weaker owing to interaction and intensity sharing with the nearby symmetric stretching mode of the mixed isotopic molecule. A very weak band at 822.6 cm^{-1} (0.0007 a) tracks with the 880.8 cm^{-1} band, and this position and intensity are appropriate for such an assignment. The B3LYP density functional typically finds a slightly higher frequency, and the 976 cm^{-1} value for CUC is in accord.[38,39]

The CASPT2 calculations with dynamical correlation find the ground state as linear $^3\Sigma_u^+$ with 1.840 Å bond length and predict a 933 cm^{-1} antisymmetric C−U−C stretching fundamental, which is corrected for anharmonicity. The $^1\Sigma_g^+$ state is higher in energy and unstable toward bending but stays comfortably higher than the triplet minimum (the bent minimum is about 3 kcal/mol higher than the linear triplet minimum). The agreement of three different computed values just above the 891.4 cm^{-1} argon matrix value confirms our identification of the linear, symmetrical CUC molecule.

(32) Frisch, M. J., et al. *Gaussian 09, Revision A.02*, Gaussian, Inc.: Wallingford, CT, 2009.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, Y.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (d) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533, and references therein.

(34) (a) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265. (b) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.

(35) Roos, B. O., The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations. In *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry - II*; Lawley, K. P., Ed.; John Wiley & Sons Ltd.: New York, 1987; Chapter 69, p 399.

(36) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(37) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575 (ANO-RCC-VTZP) basis).

(38) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(39) Andersson, M. P.; Uvdal, P. L. *J. Phys. Chem. A* **2005**, *109*, 2937–2941.

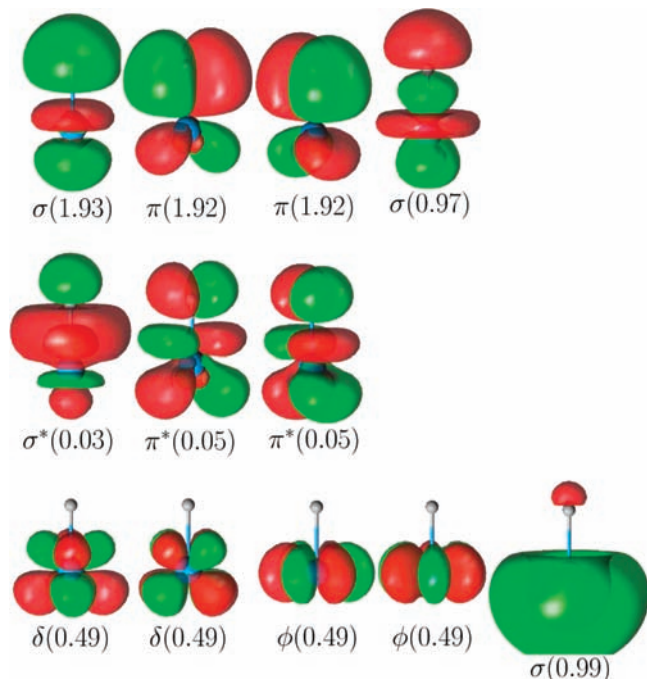(40) Jacox, M. E. *Chem. Phys.* **1994**, *189*, 149.

Figure 2. CASPT2 molecular orbitals for the quintet ($\Lambda = 5$, $\Omega = 3$) UC ground state plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

The UC and CUC bond lengths computed by three quantum chemical methods are given in Table 1. The sum of triple bond covalent radii given by Pyykkö et al.,[41] 178 pm, is slightly shorter than our three computed values.

CASPT2 molecular orbitals for quintet ($\Lambda = 5$, $\Omega = 3$) UC are plotted in Figure 2. The doubly occupied σ and σ^* and degenerate pairs of π and π^* MOs are shown in the top left corner, and the effective bond order (EBO) determined from bonding minus antibonding occupancies divided by two is 2.82, which characterizes a fully developed triple bond. The singly occupied nonbonding and atomic-like orbitals contain 3.92 electrons. Mulliken atomic spin densities computed on U and C in the UC molecule are 3.52 and 0.48: U has donated 0.48 e to C, and the resulting dipole moment is 3.94 D. Molecules with large dipole moments typically have large dipole derivatives, and they tend to have high infrared intensities, which is the case for UC.

Similar CASPT2 molecular orbitals for CUC are plotted in Figure 3. Notice two pairs of σ and σ^* and four pairs of π and π^* occupied MO's, which determine the net bonding, and the singly occupied σ and σ^* MO's, which result in a triplet ground state. The EBO is 2.83, which is comparable to that in UC. Although CUC and CUO are both U(VI) molecules, the U≡C bond in CUO is slightly shorter (1.756 Å, BPW91) and the U−C stretching frequency higher (1047.5 cm^{-1} for the singlet state in solid neon) than for CUC. This may be due in part to the slightly higher positive charge on uranium in CUO than in CUC,[42] which results in a larger ionic component and stronger bonding in CUO than in CUC. Finally, the U≡C bonds characterized here are shorter and stronger than those in simple CH≡UX$_3$ methylidyne complexes.[22]

It is interesting to compare the triple bonding in the similar molecules CUC and NUN where the latter has two more
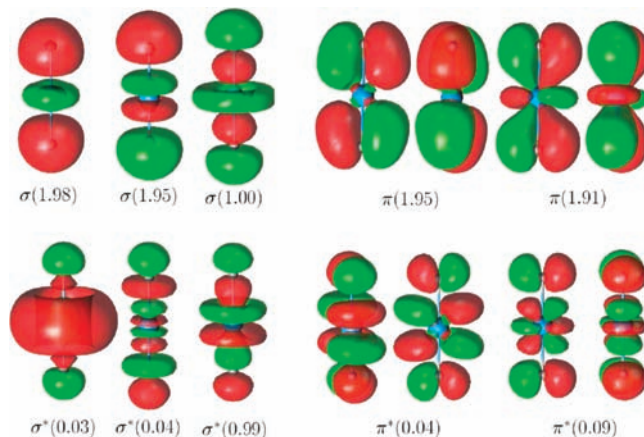

Figure 3. CASPT2 molecular orbitals for the $^3\Sigma_u^+$ CUC ground state plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

electrons, a $^1\Sigma_g^+$ ground state, and a triple bond of type $(\sigma_g)^2$ $(\sigma_u)^2$ $(\pi_g)^4$ $(\pi_u)^4$ with recently computed EBO of 2.87.[43−45] For NUN, the N 2s orbital is considered as "semicore", and the σ molecular orbitals are built from nitrogen 2p σ orbitals. However, for CUC the σ_g and σ_u molecular orbitals involve instead C 2s and not 2p. The carbon 2p orbitals appear in the half-filled, paramagnetic σ_g and σ_u molecular orbitals coupled with the uranium 6d σ and 5f σ, respectively. Qualitatively, this can be understood since carbon is lighter, and it therefore neither wants nor has so many 2p electrons.

These experiments also provide important information on the reactivity of atomic uranium. Atomic U in the ground state does not react with CO or N$_2$, but on photoexcitation, CUO or NUN are formed.[10,44] The oxygen molecule is, however, more reactive, and the U insertion with dioxygen gives OUO on annealing in a 18−24 K argon matrix.[45] Here we show that U and C atoms also react in a cold argon matrix. Laser ablation of the U/C alloy samples produces predominantly atomic species as the initial spectra show virtually no product absorptions. The atom reaction 1 clearly proceeds to form UC, and CUC is produced by the second reaction 2 with another C atom. Dicarbon, C$_2$, is probably formed on sample deposition, which is supported by the detection of C$_2$O, and we expect the insertion reaction of U with C$_2$ to be spontaneous as it is with dioxygen. The enthalpy change for reaction 3 from mass spectroscopic thermochemical data is -158 ± 3 kcal/mol.[7] Finally, the growth of C$_3$ on annealing attests to sequential carbon atom reactions in these samples.

$$U + C \rightarrow UC \qquad (1)$$

$$UC + C \rightarrow CUC \qquad (2)$$

$$U + C_2 \rightarrow CUC \qquad (3)$$

$$C + C_2 \rightarrow C_3 \qquad (4)$$
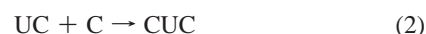
(41) Pyykkö, P.; Riedel, S; Patzschke, M. *Chem.—Eur. J.* **2005**, *12*, 3511.
(42) Mulliken atomic charges, BPW91. CUO: C,−0.74; U, 1.59; O,−0.85. CUC: U, 1.42; C,−0.71.
(43) (a) Gagliardi, L.; La Manna, G.; Roos, B. O. *Faraday Discuss.* **2003**, *124*, 63. (b) Vlaisavljevich, B.; Gagliardi, L.; Wang, X.; Liang, B.; Andrews, L.; Infante, I. To be published, 2010.
(44) Hunt, R. D.; Yustein, J. T.; Andrews, L. *J. Chem. Phys.* **1993**, *98*, 6070 (UN$_2$).
(45) Zhou, M.; Andrews, L.; Ismail, N.; Marsden, C. *J. Phys. Chem A* **2000**, *104*, 5495 (UO$_2$ in solid neon and argon).

Conclusions

We have prepared binary uranium carbon bearing molecules in optical spectroscopic quantities from U and C atom reactions and identified them from carbon-13 substitution in the matrix infrared spectrum and comparison with frequencies calculated by three quantum chemical methods. Laser-evaporated U and C atoms collected in solid argon at 8 K react directly without activation energy on warming the matrix sample to $20-30$ K and form the novel U≡C and C≡U≡C molecules with uranium−carbon triple bonds as described by CASPT2 molecular orbital calculations.

Supporting Information Available: Complete ref 32. This material is available free of charge via the Internet at http://pubs.acs.org.

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