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U and P_4 Reaction Products: A Quantum Chemical and Matrix Isolation Spectroscopic Investigation

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Reactions of laser-ablated U atoms with P_4 molecules upon codeposition in excess argon gave weak new infrared absorptions at 504, 483, and 426 cm^{-1}, which are best identified as binary uranium phosphide UP_4 species based on extensive B3LYP, BPW91, and PBE density functional and CASSCF/CASPT2 wave function based calculations. These UP_4 adducts may be considered as simple models for P_4 activation products by ligand-supported transition and main group metal complexes. The sought-after PUP molecule in the $^3\Phi_u$ ground state probably absorbs under the intense P_4 precursor band near 465 cm^{-1}. The triplet U(IV) molecule PUP is 7 kcal/mol lower in energy than the U(VI) analog, singlet PUP. The $^3\Phi_u$ ground state of PUP, with 2.54 effective bond order computed by CASPT2, may be compared to the $^1\Sigma_g^+$ ground state of $N\equiv U\equiv N$ with 2.87 effective bond order, where third row elements are less effective for π bond formation than second row elements.

Introduction

Multiple bonding between uranium and main group elements is of considerable research interest.[1−7] Uranium forms $U{=}O$ bonds in many compounds, but fewer $U{=}NX$, $U{=}PX$, and $U{=}S$ bonds are known. Imido ($An{=}NX$), phosphinidene ($An{=}PX$), and $N-U-N$ molecular linkages have been prepared,[2,3,7] and simple $NH{=}UH_2$, $N\equiv UF_3$, $P\equiv UF_3$, and US_2 molecules have been produced and identified in matrix isolation experiments and characterized by density functional theory calculations.[8−10] The simple linear $N\equiv U\equiv N$ molecule, which is isoelectronic to the uranyl dication, has been observed only by matrix isolation spectroscopy.[11,12] Although the $O{=}U{=}O$ molecule is also linear, the sulfur analog is bent, on the basis of density functional theory calculations.[10,13] Accordingly, we set out to prepare the analogous PUP molecule and to characterize its bonding and structure through quantum chemical calculations, which have been effective for the triple-bond-bearing $N\equiv UF_3$ and $P\equiv UF_3$ molecules.[9]

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The activation of white phosphorus by early and late transition metal complexes to incorporate phosphorus into organic molecules is an active field of research.[14] In particular, terminal-P_1, bridging-P_2, and cyclo-P_3 subunits have been included to form new molecules. The reaction of the weakly dimerized dithallene $(TlPhDipp_2)_2$ ($PhDipp_2$ = C_6H_3-2,6-(C_6H_3-2,6-*i*$Pr_2)_2$) with P_4 yields the thallium salt of the diaryl tetraphosphabutadienediide.[15a] Recently, osmium tetraphosphorus complexes have been prepared where P_4 tethers two different metal fragments through two phosphorus atoms.[15b] Thus, the P_4 molecule is a readily available source of this element for preparing simple binary metal phosphide molecular species without supporting ligands, and accordingly laser-ablated U atoms were reacted with P_4 molecules in matrix isolation experiments. Extensive quantum chemical calculations of possible U and P_4 reaction products were performed in this combined investigation.

Experimental and Computational Methods

Laser-ablated U atoms were reacted with P_4 in excess argon or neon during condensation at 5 K using methods described in our previous papers.[8−10,13,16,17] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating uranium target (Oak Ridge National Laboratory, high purity, depleted of ^{235}U). The uranium target was filed to remove the oxide coating and immediately placed in the vacuum chamber. White phosphorus was cut under water in a glovebag and placed into a side arm separated by a Teflon needle valve: this simple apparatus was evacuated briefly at room temperature, then P_4 was evaporated into argon or neon streams condensing on the cold window. The laser energy was varied about 10−20 mJ/pulse. FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 with 0.1 cm^{-1} accuracy using a HgCdTe range B detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to photolysis by a medium pressure mercury arc lamp (Philips, 175W) with the globe removed.

Complementary DFT calculations were performed using the Gaussian 09 program,[18] the hybrid B3LYP and pure BPW91 and PBE density functionals, and the 6-311+G(3df) basis set for phosphorus atoms and the 60 electron SDD pseudopotential for uranium.[19−22] All of the geometrical parameters were fully optimized, and the harmonic vibrational frequencies were obtained analytically at the optimized structures. Additional wave-function-based calculations were done using CASSCF/CASPT2 and the ANO-RCC-VTZP basis in order to describe the multiconfigurational nature of selected molecules and to analyze the U−P bonding in detail.[23−25] For UP, an active space comprising nine electrons in 16 orbitals (9el/16orb) was employed. The 16 orbitals are linear combinations of the U 7s, 6d, and 5f atomic orbitals with the P 3p atomic orbitals. For the PUP system, the analogous active space would have been (12el/19orbs). However, this active space is too large to be treated with current implementations of the CASSCF/CASPT2 code. We thus proceeded with a systematic truncation of the active space. We removed from the active space orbitals which are either almost doubly occupied or almost empty, and this leads us to a final active space (12el/13orb), in analogy with our prior study on NUN.[26] For a systematic comparison, we performed calculations also on NU and NUN with the same active spaces as PU and PUP. Finally, we also calculated $U(P_2)_2$ using the (12,12) active space.

Spin−orbit coupling was included using the complete active space interaction method, CASSI, which employs an effective one-electron spin−orbit (SO) Hamiltonian, based on the mean field approximation of the two electronic part.[27] This approach has been successful in studying many actinide-containing systems.[28] Effective bond orders, EBO, were calculated as bonding minus antibonding occupancies divided by two.

Results

Infrared spectra of laser-ablated uranium atom reaction products with P_4 in excess argon and neon during condensation at 5 K will be presented in turn. Extensive density functional and CASSCF/CASPT2 calculations were performed to characterize possible reaction products, to support their identification, and to explore the bonding in new reaction products. Weak absorptions for common species, such as P_4O at 1241 cm^{-1} and uranium dioxide at 776 cm^{-1}, have been identified in previous papers.[13,17]

Infrared Spectra of U + P_4 Reaction Products. Representative infrared spectra of laser-ablated uranium atom reaction products with P_4 evaporating at room temperature into a condensing excess argon stream illustrated in Figure 1a−d reveal the strong P_4 fundamental at 465 cm^{-1} with a splitting at 461 cm^{-1}, and a weaker band at 610 cm^{-1} is not shown, which is the same as reported previously.[17] Weak, new absorptions were observed at 504, 483, and 426 cm^{-1}. The 504 cm^{-1} band decreased slightly on annealing and was unchanged by >220 nm

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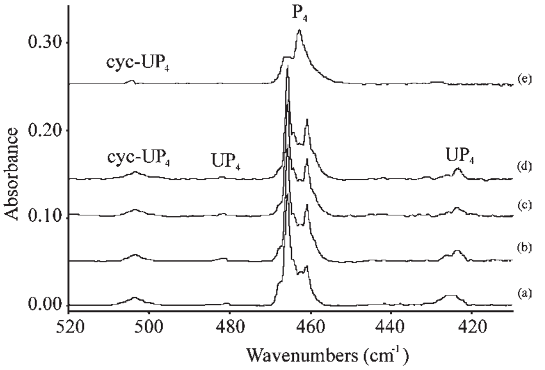

Figure 1. Infrared spectra of uranium and P_4 reaction products. (a) U and P_4 codeposited in excess argon at 5 K for 60 min, (b) after annealing to 22 K, (c) after >220 nm irradiation for 20 min, and (d) after annealing to 30 K. (e) U and P_4 codeposited in excess neon at 5 K for 60 min. The UP_4 label represents structure 1, and the cyc-UP_4 label represents isomer structure 7, as illustrated in Figure 2.

Table 1. Calculated Structural Parameters and Harmonic Frequencies for UP and UP_2[a]

molecule	CASPT2	B3LYP	BPW91	PBE
UP	2.38[b]	2.38	2.33	2.33
$^4\Gamma$	484 (43)	405 (64)	425 (44)	428 (43)
PUP	2.31/180[b]	2.28/156	2.31/129	2.31/126
$^1\Sigma_g^+$	523 (σ_u, 65)	485 (b_2, 139)	455 (b_2, 59)	468 (41)
	459 (σ_g, 0)	464 (a_1, 1)	431 (a_1, 4)	434 (4)
	142 (π_u, 10 × 2)	46 (a_1, 23)	43 (a_1, 6)	46 (5)
$^3\Phi_u$	2.36/180[b]	2.33/180	2.34/180	2.34/180
	489 (σ_u, 7)	468 (σ_u, 92)	457 (σ_u, 84)	458 (85)
	427 (σ_g, 0)	420 (σ_g, 0)	412 (σ_g, 0)	413 (0)
	131 (π_u, 17 × 2)	49(π_u, 30 × 2)	59(π_u, 25 × 2)	47 (28 × 2)

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

irradiation, and the latter decreased in favor of a satellite absorption at 424 cm^{-1} on annealing to 22 K and then decreased on >220 nm irradiation and increased slightly on final annealing to 28 K.

A similar experiment in condensing neon gave P_4 absorptions at 607 and 463 cm^{-1} with weak new reaction product counterpart bands at 505 and 428 cm^{-1}, which are shown in Figure 1e.

Calculations on UP, PUP, UP_3, UP_4 Isomers and $P_{2,3,4}$. Computations were done first at the density functional level and then with the CASSCF/CASPT2 method, and the results are summarized in Table 1. While doublet, quartet, and sextet states were explored, the ground state for UP is a $\Omega = 1.0$ state and is dominated by quartet states as found in CASSI calculations. The state with the largest contributions are 47% from the $^4\Gamma$; and 32% from the $^4\Phi$ states. Since theses states have the largest contribution to the SO ground state, we calculated the fundamental frequencies for both cases. The $^4\Gamma$ and $^4\Phi$ frequencies were very close at 484 cm^{-1} and 481 cm^{-1} respectively, both being higher with the CASSCF/CASPT2 method. A linear triplet is the ground state for PUP, which is 7 kcal/mol lower in energy than the lowest energy [linear] singlet at the CASSCF/CASPT2 level. Since the singlet and triplet states are close in energy, a CASSI calculation was performed confirming that the spin−orbit ground state is a mixture of triplets. The state described in the bonding section contributes to 95% of the spin−orbit state. The B3LYP and BPW91 and PBE approximations find the triplet lower than the singlet by 19 and 16 kcal/mol, respectively. The important, intense diagnostic antisymmetric P−U−P stretching fundamental for triplet PUP is calculated at 489, 468, and 457 cm^{-1} for the three methods, and the computed bond lengths are compared in Table 1 and with nitrogen analogs in Table 2. The antisymmetric P−U−P stretching fundamental for singlet PUP is calculated at 523, 485, and 455 cm^{-1} for the three methods. Interestingly, the lowest quintet cyclic U(PP) isomer is 13 kcal/mol lower in energy than triplet PUP at the PBE level. The cyclic isomer has 466 cm^{-1} (52 km/mol intensity), 314 (1), and 282 (1) frequencies and 2.538 Å U−P and 2.150 Å P−P bond lengths. However, the quintet U(NN) triangular molecule, with 2.093 Å U−N and 1.290 Å N−N bond lengths, is 66 kcal/mol higher in energy than the observed singlet, linear NUN molecule.[11,12]

Table 2. Comparison of Electronic States, Bond Orders, and Distances For Uranium Pnictides

system	electronic state	effective bond order	bond distance in Å
PUP	$^3\Phi_u$	2.54	2.36
PUP	$^1\Sigma_g^+$	2.75	2.31
PU	$^4\Gamma$	2.76	2.38
NUN	$^1\Sigma_g^+$	2.87	1.73
NU	$^4\Gamma$	2.85	1.76

UP_3 has a quartet state pyramidal structure with the strongest infrared fundamental computed at 475 cm^{-1}.

The UP_4 geometries explored are illustrated in Figure 2. Structure 1 is the global energy minimum in the triplet state, while the quintet state is 8−15 kcal/mol higher and the singlet much higher. Its two strongest infrared bands are 484 cm^{-1} (10 km/mol) and 420 cm^{-1} (15 km/mol) using the PBE functional. Next, the bicyclic $U(P_2)_2$ isomer of UP_4 is a C_{2v} structured $^3B_2$ state (U−P = 2.57 Å, P−P = 2.08 Å, P−U−P angles 104°, 84°), given as structure 3 in Figure 2, which is some 15−17 kcal/mol higher with the strongest IR active modes at 548 cm^{-1} (29 km/mol) using PBE/TZVPP. Calculations were performed at the CASSCF/CASPT2 level with the ANO-RCC-VTZP basis sets in C_{2v} symmetry. A (12,12) active space was chosen. Singlet and triplet spin states were considered. The ground state at the CASPT2 level was also the $^3B_2$ state. The cyclic-UP_4 isomer, structure 7 in Figure 2, is 13 or 18 kcal/mol higher in energy (Table 3). Geometry 5 is 22 kcal/mol higher in energy, and structures 2 and 4 have one imaginary frequency and are about 20 kcal/mol higher than the global minimum.

For calibration the singlet P_2 and P_4 molecules were computed using density functional methods. The computed P_2 values [B3LYP, 812 cm^{-1}, 1.888 Å; BPW91, 782 cm^{-1}, 1.903 Å; PBE, 784 cm^{-1}, 1.904 Å] may be compared to those measured for the gaseous molecule [775 cm^{-1}, 1.894 Å].[29] And the computed P_4 values [B3LYP, 607 cm^{-1} (a_1, 0 km/mol), 460 cm^{-1} (t_2, 0.3 × 3), 367 cm^{-1} (e, 0 × 2), 2.205 Å; BPW91, 599 cm^{-1} (a_1, 0 km/mol), 459 cm^{-1} (t_2, 0.2 × 3), 369 cm^{-1} (e, 0 × 2), 2.211 Å; PBE, 603 cm^{-1} (a_1, 0 km/mol), 462 cm^{-1}

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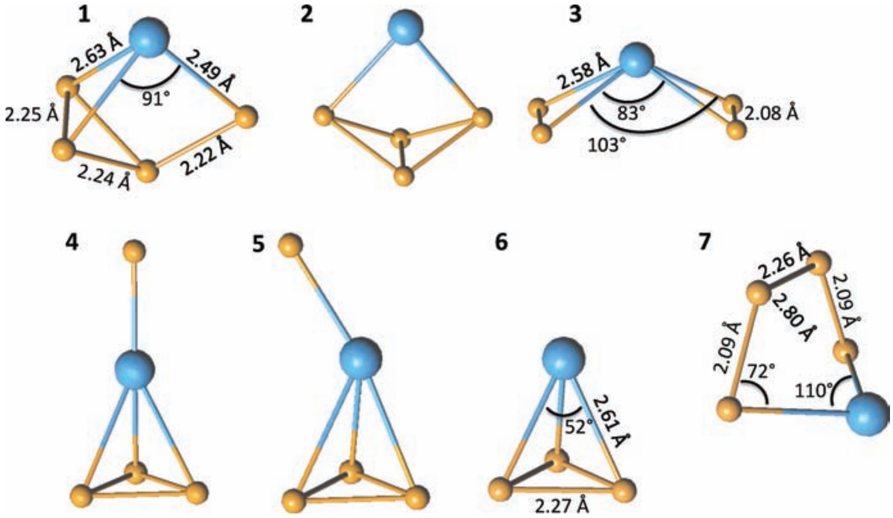

Figure 2. Structures considered for the reaction product of U atoms with P_4.

Table 3. Computed Energies for U and P_4 Reaction Products

DFT: U(SDD) P(6-311+G(3df)) CAS: ano-rcc-vtzp

reaction	level of theory	ΔE (kcal/mol) (products − reactants)
$U + P_4 \rightarrow PUP + P_2$	B3LYP	10.7
	PBE	1.2
	CASPT2	10.2
$U + P_2 \rightarrow PUP$	B3LYP	−35.1
	PBE	−62.7
	CASPT2	−44.8
$U + P_4 \rightarrow UP + P_3$	B3LYP	40.8
	PBE	22.5
	CASPT2	49.3
$U + P_2 \rightarrow UP + P$	B3LYP	50.9
	PBE	24.3
	CASPT2	32.5
$U + P_2 \rightarrow U(PP)$	B3LYP	−59.1
	PBE	−75.5
$U + P_3 \rightarrow UP_3$	B3LYP	−100.8
	PBE	−117.1
$U + P_4 \rightarrow UP_3 + P$	B3LYP	4.6
	PBE	2.1
$U + P_4 \rightarrow UP_4$ (struct. 1)	B3LYP	−75.1
	PBE	−93.1
$U + P_4 \rightarrow UP_4$ (struct. 3)	B3LYP	−60.0
	PBE	−75.6
$U + P_4 \rightarrow UP_4$ (struct. 7)	B3LYP	−62.5
	PBE	−74.9

(t_2, 0.2 × 3), 372 cm^{-1} (e, 0 × 2), 2.208 Å] are near those measured for the gaseous molecule [601, 466, 361 cm^{-1}; 2.21 Å].[30,31] The P_3 radical ground state has been computed to have an almost isosceles triangular structure, and an argon matrix electronic spectrum has been assigned.[29,30] Our computed P_3 radical $^2A_2$ ground state values [B3LYP, 631 cm^{-1} (a_1, 0 km/mol), 403 cm^{-1} (a_1, 1), 218 cm^{-1} (b_2, 34), 2.225, 2.079 Å; BPW91, 621 cm^{-1} (a_1, 0 km/mol), 402 cm^{-1} (a_1, 1), 267 cm^{-1} (b_2, 31), 2.259, 2.089 Å; PBE, 624 cm^{-1} (a_1, 0 km/mol), 405 cm^{-1} (a_1, 1), 271 cm^{-1} (b_2, 32), 2.257, 2.088 Å] suffer from too low IR intensity, as a comparison with P_4 illustrates.

Energetics provide a useful guide for the reactions to be expected in this system, and energies from density functional and a few CASPT2 calculations are given in Table 3, as such density functional calculations have found considerable application for uranium bearing molecules.[9,32−34] These reaction energies are only approximate, as spin−orbit coupling is not included. The most exothermic primary reaction gives structure 1.

$$U + P_4 \rightarrow UP_4 \quad \Delta E \sim -90 \text{ kcal/mol [PBE]} \qquad (1)$$

$$U + P_2 \rightarrow PUP \quad \Delta E \sim -60 \text{ kcal/mol [PBE]} \qquad (2)$$

Assignments of the Matrix Spectra. The most favorable reaction energetically is to form the adduct structure 1 (Figure 2). The strongest PBE computed frequencies, 484 cm^{-1} (10 km/mol) and 420 cm^{-1} (15 km/mol), are within 6 cm^{-1} of the argon matrix values, and for such a complicated molecule, this agreement is sufficient to support assignment of the weak 483 and 426 cm^{-1} bands to structure 1. The next most favorable reaction is to form the cyclic-UP_4 molecule, structure 7. Its strongest calculated frequency, an antisymmetric P−P═P stretching mode, at 523 cm^{-1} (18 km/mol) is slightly higher than the 504 cm^{-1} observed frequency, which is in the range of agreement expected for density functional theory. [All computed frequencies for these molecules are listed in the Supporting Information.] Thus, the best assignment for the 504 cm^{-1} band is the cyclic-UP_4 species. The calculated P−P bond lengths for our structure 7, 2.09, 2.26, and 2.09 Å, bracket the 2.136, 2.143 Å values measured for the dithallium complex.[15a] Finally, the $U(P_2)_2$ adduct, structure 3, which is a bis-diphosphorus complex, is of comparable stability, but the strongest computed antisymmetric P−P stretching frequency, 548 cm^{-1}, is too far above the 504 cm^{-1}

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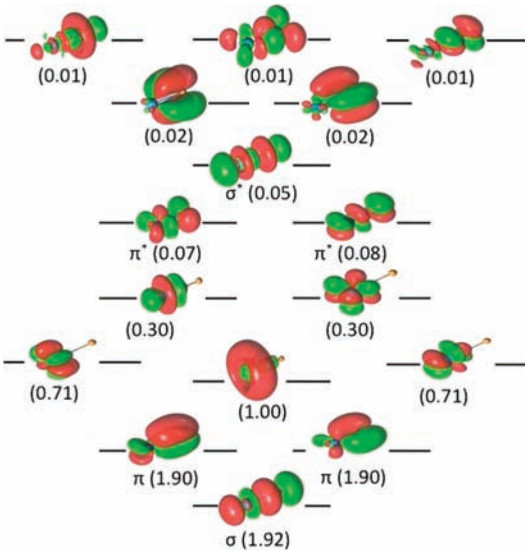

Figure 3. CASPT2 molecular orbitals for the major quartet spin−orbit component of the UP ground state plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

value to make this assignment. This bis-diphosphorus complex is of interest as no such transition metal analogs appear to be known.[14]

Tetraphosphorus decomposes thermally to diphosphorus above 800 °C,[31] and it is likely that vacuum ultraviolet radiation in the laser ablation plume will effect some such photodissociation during our sample deposition. The exothermic insertion reaction 2 may contribute to the product yield, but our calculations suggest that the triplet ground state PUP absorption probably falls under the very strong P_4 precursor band where it cannot be observed. Even the slightly more stable cyclic-UP_2 isomer would probably absorb under the P_4 precursor band, based on its strongest computed frequency.

Comparison Calculations on UN and NUN. Calculations were also done for UN and NUN for differences in first and second row element bonding with uranium. Doublet, quartet, and sextet states were considered for NU, and $^2\Gamma$, $^2\Phi$, $^4\Gamma$, and $^4\Phi$ were lowest. At the CASPT2 level, $^4\Gamma$ was the ground state with $^4\Phi$ 3.4 kcal/mol higher. The converged bond length was 1.757 Å and the frequency was 1034 cm^{-1} (275 km/mol intensity) for the $^4\Gamma$ ground UN state, which compare to 1.733 Å and 1095 cm^{-1} (521 km/mol), 1037(0), and 80(49) for NUN. To date, these molecules have only been observed in solid matrices, and the frequencies compare favorably with observations [UN, 1001 cm^{-1} in Ar; NUN, 1051 cm^{-1} in Ar and 1076 cm^{-1} in Ne][11,12,34] and earlier calculations.[13,26,34]

Structure and Bonding in Uranium Phosphides. The bond lengths of the small uranium phosphide molecules investigated here are given in Table 1. The hybrid density functional bond lengths are longer and suggest that this functional underestimates the U−P bonding. The CASSCF/CASPT2 molecular orbitals with occupation numbers for the major quartet component of ground state UP are representative of the ground state and are shown in Figure 3. The unpaired electrons are in 10 partially occupied MOs, which are localized mostly on the uranium atom. The remaining bonding and antibonding σ and π molecular orbitals give an effective bond order (EBO) of 2.76 for $^4\Gamma$ ground state of $U{\equiv}P$. Our computed bond lengths for UP are much closer to the sum of double bond radii (236 pm) than triple bond radii (212 pm) given by Pyykkö et al.[36] The ground $^3\Phi_u$ PUP electronic state MOs are given in Figure 4. The EBO is higher, 2.75, for the higher energy singlet state, than for the lower energy triplet state, 2.54. The five bonding MOs for the triplet state are located at the bottom of Figure 4, and one SOMO shown in the middle is localized on U and the other is σ bonding. The MOs for singlet PUP are displayed in Figure 5 and may be compared with those of singlet NUN below.

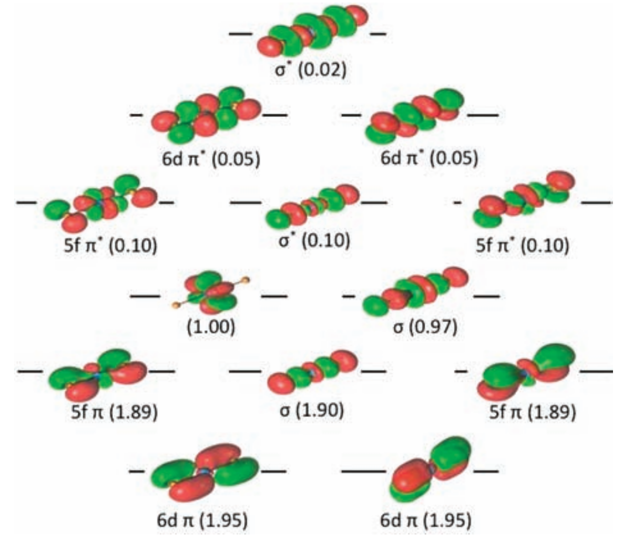

Figure 4. CASPT2 molecular orbitals, (12,13) active space, for the $^3\Phi_u$ state of PUP plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

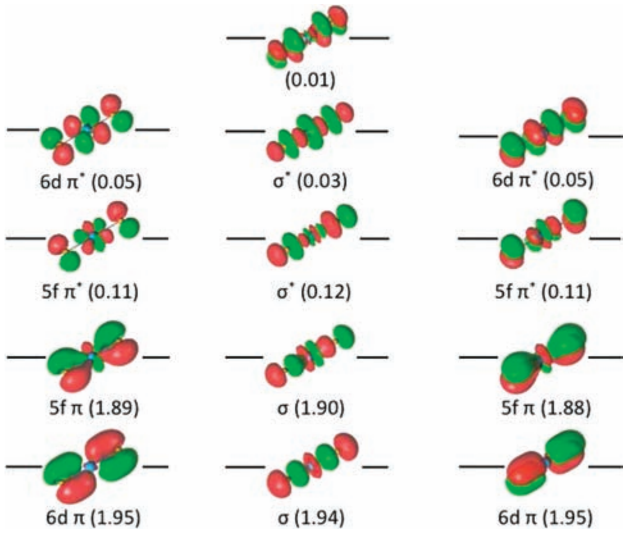

Figure 5. CASPT2 molecular orbitals, (12,13) active space, for the $^1\Sigma_g^+$ state of PUP plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

Analogous CASPT2 computations were performed on UN and NUN for reference. The $^4\Gamma$ ground state UN molecule has a 2.85 EBO, and the linear $^1\Sigma_g^+$ ground state

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(36) (a) Pyykkö, P.; Riedel, S.; Patzschke, M. *Chem.—Eur. J.* **2005**, *11*, 3511. (b) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770.

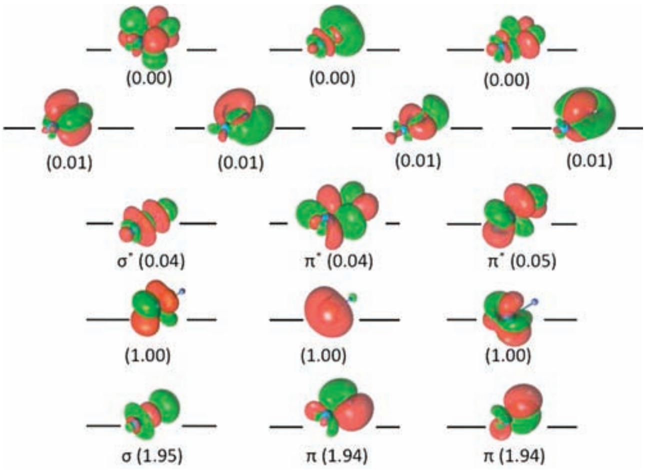

Figure 6. CASPT2 molecular orbitals for the $^4\Gamma$ ground state of UN plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

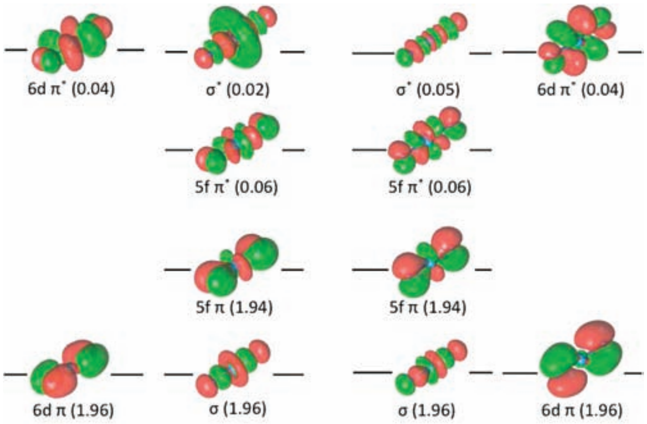

Figure 7. CASPT2 molecular orbitals for the $^1\Sigma_g^+$ state ground state of NUN plotted using an isodensity of 0.04 e au^{-3}. Occupation numbers are given in parentheses.

NUN molecule has almost the same EBO, 2.87. The UN molecular orbitals are plotted in Figure 6: the three unpaired electrons are localized on the uranium center, σ and π bonding MOs are occupied, and the seven highest MOs have virtually no electron occupancy. For NUN, the σ and π bonding and antibonding MO sets are illustrated in Figure 7. Both nitrides have fully developed triple bonds, which have slightly higher effective bond orders than the phosphorus analogs.

Overall, the nitrides have a slightly higher bond order compared to the corresponding phosphorus analogs. A close inspection of the natural orbital occupation numbers for singlet NUN and PUP shows that the main difference between the two species concerns the 5f π orbitals, which have an occupation number of 1.94 in the NUN case, and only 1.89 in the PUP case. The corresponding antibonding orbitals have a larger occupation number in PUP than in NUN, which results in a slightly higher effective bond order for the dinitride. In addition, there may be a partial loss of covalent bonding to the more compact uranium 5f σ_u and π_u orbitals by the more diffuse phosphorus 3p orbitals, compared to nitrogen 2p.

Conclusions

Reactions of laser-ablated U atoms with P_4 molecules upon condensation in excess argon appear to form two stable UP_4 adducts, based on a comparison of calculated and observed frequencies. The structures and relative energies of these adducts have been explored by extensive density functional calculations. These UP_4 adducts may be considered as simple models for P_4 activation products by ligand-supported transition and main group metal complexes.[14,15]

The anticipated triplet PUP reaction product absorption would likely be covered by the strong P_4 precursor band. The $^3\Phi_u$ ground state of PUP, with 2.54 effective bond order computed by CASPT2, is a U(IV) molecule. The higher energy U(VI) $^1\Sigma_g^+$ state of P≡U≡P, with a 2.75 effective bond order computed by CASPT2, may be compared the $^1\Sigma_g^+$ ground state of N≡U≡N with a 2.87 effective bond order, where third row elements are less effective for π bond formation than second row elements. The major quartet ground state component of U≡P, which has a 2.76 effective bond order, may be compared with the $^4\Gamma$ ground state of U≡N, which has a 2.85 effective bond order. A similar relationship with a more pronounced difference has been found for the N≡UF_3 and P≡UF_3 molecules with 2.78 and 2.39 EBO, respectively.[9]

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Supporting Information Available: Structure and MOs for $U(P_2)_2$. Table of computed frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.