# Infrared spectra and density functional calculations of triplet pnictinidene $N \div ThF_3$ , $P \div ThF_3$ and $As \div ThF_3$ molecules

Xuefeng Wang and Lester Andrews\*

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Thorium atoms react with NF<sub>3</sub>, PF<sub>3</sub>, and AsF<sub>3</sub> to produce the first actinide triplet state pnictinidene molecules, N÷ThF<sub>3</sub>, P÷ThF<sub>3</sub>, and As÷ThF<sub>3</sub>, which are trapped in solid argon and identified from infrared spectra and comparison to computed vibrational frequencies. Density functional theory calculations for these lowest energy triplet state products converge essentially to  $C_{3v}$  symmetry structures. Spin density calculations show that the two unpaired electrons are mostly localized in nitrogen 2p, phosphorus 3p, or arsenic 4p orbitals. Although thorium has a small spin density, the weak degenerate  $\pi_{\alpha}$  molecular orbitals are populated entirely from the terminal N, P, or As based on DFT natural bond orbital analysis. This is in contrast with HC÷ThF<sub>3</sub>, which contains degenerate  $\pi_{\alpha}$ molecular orbitals with 81% C and 19% Th character.

## Introduction

The simple nitrenes CH<sub>3</sub>-N and CF<sub>3</sub>-N are reactive triplet state intermediates.<sup>1,2</sup> A characteristic reaction of alkyl nitrenes is substituent rearrangement to give the lower energy imine.<sup>3</sup> Methylene imine  $CH_2 = NH$  is the more stable isomer of triplet CH<sub>3</sub>-N.<sup>4,5</sup> In reactions of group 4 metal atoms with ammonia, the lower energy MH<sub>2</sub>=NH imine analogs were formed, but reactions with NF<sub>3</sub> gave instead the triplet state nitrene species MF<sub>3</sub>-N, which is lower in energy owing to the formation of stronger M-F bonds.<sup>6-8</sup> Analogous reactions of Th atoms with ammonia produced thorimine,  $ThH_2 = NH$ , and the higher energy triplet thorium nitrene, ThH<sub>3</sub>-N, was not formed.<sup>9</sup> The reaction of uranium atoms with NH<sub>3</sub> behaved similarly to give UH<sub>2</sub>=NH, but U reacted with NF<sub>3</sub> and PF<sub>3</sub> to produce the higher oxidation state and lower energy terminal nitrides UF<sub>3</sub>≡N and UF<sub>3</sub>≡P.<sup>10,11</sup> Accordingly, we wish to investigate the Th reaction with NF<sub>3</sub> in an attempt to form the first terminal actinide nitrene derivative ThF<sub>3</sub>-N, and we report here matrix infrared spectra and density functional calculations on the new series of thorium based pnictinidene products of thorium atom reactions with NF<sub>3</sub>, PF<sub>3</sub> and AsF<sub>3</sub>.

## Experimental and computational methods

Laser ablated Th atoms (Oak Ridge National Laboratory) were reacted with NF<sub>3</sub> (Matheson), PF<sub>3</sub> (PCR Research), or AsF<sub>3</sub> (Ozark-Mahoning, vacuum distilled from dry NaF) in excess argon and neon during condensation at 5 K using the closedcycle refrigerator described elsewhere.<sup>12,13</sup> Reagent gas mixtures were typically 0.5% in argon. After the reaction with thorium, infrared spectra were recorded at a resolution of 0.5 cm<sup>-1</sup> using a Nicolet 750 spectrometer with a Hg–Cd–Te range B detector. Samples were later irradiated for 15 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination

Department of Chemistry, University of Virginia, P.O Box 400319, Charlottesville, Virginia 22904-4319. E-mail: lsa@virginia.edu of optical filters, and then samples were annealed to allow reagent diffusion and further reaction.

Following our work on reactions with the isoelectronic fluoroform molecule,<sup>14</sup> theoretical computations were performed using the Gaussian 03 program with the B3LYP hybrid and BPW91 density functionals.<sup>15-17</sup> The 6-311+G(3df) basis was used to represent the electronic density of nitrogen, fluorine, phosphorus and arsenic atoms and SDD pseudopotential and basis for thorium.<sup>18,19</sup> Frequencies were computed analytically, and all energy values reported include zero-point vibrational corrections. Natural bond orbital analysis was also performed for the product molecules.<sup>15,20</sup>

# **Results and discussion**

Infrared spectra of products formed in the reactions of laserablated thorium atoms with NF<sub>3</sub>, PF<sub>3</sub>, and AsF<sub>3</sub> in excess argon during condensation at 5 K will be presented in turn. Density functional calculations were performed to support the identifications of new reaction products. Bands common to experiments using different laser ablated metals with NF<sub>3</sub> [such as NF<sub>2</sub> and NF<sub>2</sub><sup>-</sup>], with PF<sub>3</sub> [PF<sub>2</sub>, PF<sub>5</sub>, and PF<sub>2</sub><sup>-</sup>], and with AsF<sub>3</sub> [AsF<sub>2</sub> and AsF<sub>5</sub>] have been identified previously and will not be mentioned again here.<sup>21,22</sup>

## Infrared spectra

Matrix infrared spectra for Th reactions with NF<sub>3</sub> in excess argon are compared in Fig. 1. The sharp bands at 525.6, 520.9, and 514.6 cm<sup>-1</sup> in the spectra have been reported previously and assigned to thorium tetrafluoride in solid argon.<sup>23</sup> The latter product absorptions were also observed after the laser-ablated Th atom reaction in separate experiments with argon/fluorine samples. The major new product absorptions for Th and NF<sub>3</sub> are at 575.5, 525.2, and 430.0 cm<sup>-1</sup>. These bands increase together on UV irradiation doubling their absorbance (Fig. 1(a)–(d)) while a minor set of bands closely positioned at 565.0, and 531.0 cm<sup>-1</sup> is almost destroyed on the same irradiation sequence. Subsequent



**Fig. 1** Infrared spectra for thorium atom reaction products with NF<sub>3</sub> in excess argon in the 580–420 cm<sup>-1</sup> region. (a) Spectrum after co-deposition of laser-ablated Th and NF<sub>3</sub> at 0.4% in argon at 5 K for 60 min, (b) after annealing to 20 K, (c) after 240–380 nm irradiation, (d) after >220 nm irradiation for 20 min, and (e) after annealing to 30 K.

annealing to 35 K slightly decreased the absorptions. Reducing the sample concentration from 0.4 to 0.2% decreased the relative yield of ThF<sub>4</sub> in the spectrum but had no effect on the photochemistry. An experiment with 0.1% NF<sub>3</sub> in neon and lower laser energy gave weaker bands for ThF<sub>4</sub> at 534.1 and 529.3 cm<sup>-1</sup> and a weak new 536.1 cm<sup>-1</sup>, which increased on UV irradiation like the 525.3 cm<sup>-1</sup> argon matrix band.

Infrared spectra for the corresponding Th atom reactions with PF<sub>3</sub> are illustrated in Fig. 2. The ThF<sub>4</sub> bands were much weaker as PF<sub>3</sub> is a more stable compound than NF<sub>3</sub>. The major Th reaction product at 528.3 cm<sup>-1</sup> has a 531.3 cm<sup>-1</sup> satellite and these are joined by weaker bands at 569.1 and 566.3 cm<sup>-1</sup>. These bands sharpen on annealing to 20 K and increase 10% on >290 nm irradiation, but >220 nm irradiation increases the 528.3 and 569.1 cm<sup>-1</sup> bands 20% and decreases the 531.3 and 566.3 cm<sup>-1</sup> bands a like amount,



**Fig. 2** Infrared spectra for thorium atom reaction products with  $PF_3$  in excess argon and neon in the 580–500 cm<sup>-1</sup> region. (a) Spectrum after co-deposition of laser-ablated Th and  $PF_3$  at 0.4% in argon at 5 K for 60 min, (b) after annealing to 20 K, (c) after >290 nm irradiation for 20 min, (d) after >220 nm irradiation, (e) after annealing to 30 K, and (f) after annealing to 35 K, (g) spectrum after co-deposition of laser-ablated Th and  $PF_3$  at 0.3% in neon at 5 K for 60 min, (h) after >240–380 nm irradiation for 20 min, and (i) after annealing to 12 K.

traces (a)–(d). Annealing to 30 K increases the second pair of bands more, and further annealing to 35 K holds the second pair and decreases the first pair about 20% (spectra (e),(f)).

The neon matrix spectrum for Th and PF<sub>3</sub> (0.3%) is compared in Fig. 2, traces (g)–(i). The major ThF<sub>4</sub> bands are again at 534.1 and 529.3 cm<sup>-1</sup>, and a weak new absorption appears at 539.8 cm<sup>-1</sup> with a 542.6 cm<sup>-1</sup> shoulder along with an even weaker band at 567.9 cm<sup>-1</sup> with a 566.5 cm<sup>-1</sup> shoulder. Ultraviolet photolysis increases these bands slightly, and annealing to 12 K favors the inside pair relative to the outside pair, similar to the argon matrix observations.

Spectra for Th reactions with  $AsF_3$  are shown in Fig. 3. The ThF<sub>4</sub> bands are stronger than with PF<sub>3</sub> but weaker than when produced by the NF<sub>3</sub> reaction. Stronger bands are observed at 532.0 and 528.9 cm<sup>-1</sup> with weaker associated bands at 569.5 and 566.9 cm<sup>-1</sup>. Ultraviolet irradiation and annealing alter these four bands in like fashion to that described above and associate the inner and outer pairs accordingly.



**Fig. 3** Infrared spectra for thorium atom reaction products with AsF<sub>3</sub> in excess argon in the 580–500 cm<sup>-1</sup> region. (a) Spectrum of argon–arsenic trifluoride precursor, (b) spectrum after co-deposition of laser-ablated Th and AsF<sub>3</sub> at 0.4% in argon at 5 K for 60 min, (c) after annealing to 20 K, (d) after >320 nm irradiation for 20 min, (e) after >220 nm irradiation for 20 min, and (f) after annealing to 30 K.

#### Calculations

Density functional theory calculations were done for potential reaction product structures, energies, and vibrational frequencies. Following previous investigations with these  $EF_3$  (E = N, P, As) precursors,<sup>8,21</sup> we expect reactions (1), (2), and (3) to occur.

$$Th(^{3}F) + NF_{3} \rightarrow F_{2}N - ThF \rightarrow FN = ThF_{2} \rightarrow N \div ThF_{3}$$
 (1)

$$Th(^{3}F) + PF_{3} \rightarrow F_{2}P - ThF \rightarrow FP = ThF_{2} \rightarrow P \div ThF_{3}$$
 (2)

$$Th(^{3}F) + AsF_{3} \rightarrow F_{2}As - ThF \rightarrow FAs = ThF_{2} \rightarrow As \div ThF_{3}$$
 (3)

Our B3LYP calculations find these overall reactions to be exothermic as the final triplet state products are 340, 169, and 215 kcal mol<sup>-1</sup> lower in energy than the reagents, respectively. An attempt to calculate the first step in reaction (1), singlet  $F_2N$ -ThF, converged instead to the second step, singlet FN=ThF<sub>2</sub>, which is 39 kcal mol<sup>-1</sup> higher in energy than the final triplet

**Table 1** Observed and calculated fundamental frequencies for the  $N \div ThF_3$  nitrene complex in the  ${}^{3}A''$  ground electronic state with approximate  $C_{3v}$  symmetry<sup>*a*</sup>

Approx. mode <sup>b</sup>	$N \div ThF_3$				
Description	Obs <sup>c</sup>	Calc(B3)	Int	Calc(BP)	Int
Th-F str, $a_1$ Th-F str, $e$ N÷Th str, $a_1$ ThF <sub>3</sub> def, $e$ ThF <sub>3</sub> def, $a_1$	575.5 525.2 430.0	573 533 454 117 111	$34$ $212 \times 2$ $100$ $10 \times 2$ $28$ $22 \times 2$	565 528 446 115 104	$34 \\ 200 \times 2 \\ 84 \\ 10 \times 2 \\ 17 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 2$

<sup>*a*</sup> Frequencies and intensities are in cm<sup>-1</sup> and km mol<sup>-1</sup>. Frequencies and intensities computed with B3LYP and BPW91/6-311+G(3df) in the harmonic approximation using the SDD core potential and basis set for metal atoms. <sup>*b*</sup> The mode symmetry notations are based on the  $C_{3v}$ structure. The degenerate modes were split 1 to 3 cm<sup>-1</sup>, and average values are reported here. <sup>*c*</sup> Observed in an argon matrix. Argon matrix site absorptions at 569.0 and 531.3 cm<sup>-1</sup>. Neon matrix counterpart for strongest band at 536.1 cm<sup>-1</sup>.

**Table 2** Observed and calculated fundamental frequencies for the  $P \div ThF_3$  complex in the <sup>3</sup>A" ground electronic S state with approximate  $C_{3v}$  symmetry<sup>*a*</sup>

Approx. mode <sup>b</sup>	$P \div ThF_3$				
Description	Obs <sup>c</sup>	Calc(B3)	Int	Calc(BP)	Int
Th–F str. a <sub>1</sub>	569.1	573	81	562	75
Th-F str, e	528.3	539	$190 \times 2$	532	$178 \times 2$
$P \div Th$ str. $a_1$		256	33	255	29
ThF <sub>3</sub> def, e		114	$11 \times 2$	104	$9 \times 2$
ThF <sub>3</sub> def, $a_1$		108	10	97	13
P–Th–F def, e		86	$9 \times 2$	78	$7 \times 2$

<sup>*a*</sup> Frequencies and intensities are in cm<sup>-1</sup> and km mol<sup>-1</sup>. Frequencies and intensities computed with B3LYP and BPW91/6-311+G(3df) in the harmonic approximation using the SDD core potential and basis set for metal atoms. <sup>*b*</sup> The mode symmetry notations are based on the  $C_{3v}$ structure. Using B3LYP the degenerate modes were split 3 to 6 cm<sup>-1</sup>, and average values are reported here, but BPW91 gave degenerate modes and identical bond lengths. <sup>c</sup> Observed in an argon matrix. Argon matrix site absorptions at 566.3 and 531.3 cm<sup>-1</sup>. Neon matrix counterparts at 567.9 and 539.8 cm<sup>-1</sup> with shoulders at 566.5 and 542.4 cm<sup>-1</sup> for matrix sites.

state N÷ThF<sub>3</sub> product. Furthermore, the singlet state N–ThF<sub>3</sub> is computed to be 41 kcal mol<sup>-1</sup> higher energy than the triplet state, which is comparable to the 44 kcal mol<sup>-1</sup> triplet–singlet separation computed for N–CF<sub>3</sub>.<sup>2</sup> In like fashion, the second step FP=ThF<sub>2</sub> molecule is 43 kcal mol<sup>-1</sup> higher in energy than the final P÷ThF<sub>3</sub> product of reaction (2), and the second step FAs=ThF<sub>2</sub> is 60 kcal mol<sup>-1</sup> higher in energy than the final As÷ThF<sub>3</sub> product of reaction (3). In marked contrast with reaction (1), the reaction with ammonia produced the singlet thorimine HN=ThH<sub>2</sub> final product,<sup>9</sup> and the triplet nitrene N÷ThH<sub>3</sub> is 86 kcal mol<sup>-1</sup> higher in energy owing to the relative strengths of the N–H and Th–H bonds. The analogous relationship is found for the isoelectronic reactive HN=CH<sub>2</sub> and N÷CH<sub>3</sub> species, where the nitrene is computed to be 50 kcal mol<sup>-1</sup> higher energy than the imine using B3LYP.

The triplet state final product structures were calculated at the B3LYP and BPW91 levels of theory, the frequencies are listed in Tables 1–3, and the structural parameters are given in Table 4. Notice that the two density functionals predict the frequencies no more than 14 cm<sup>-1</sup> apart, and the B3LYP values are higher

**Table 3** Observed and calculated fundamental frequencies for the  $As \div ThF_3$  complex in the <sup>3</sup>A" ground electronic state with approximate  $C_{3v}$  symmetry<sup>*a*</sup>

Approx. mode <sup>b</sup>	$As \div ThF_3$				
Description	Obs <sup>c</sup>	Calc(B3)	Int	Calc(BP)	Int
Th–F str, a <sub>1</sub>	569.5	573	90	562	82
Th–F str, e	528.9	539	$183 \times 2$	533	$173 \times 2$
As÷Th str, $a_1$		177	23	174	18
ThF <sub>3</sub> def, e		113	$10 \times 2$	104	$10 \times 2$
ThF <sub>3</sub> def, $a_1$		107	10	93	9
As-Th-F def, e		81	$6 \times 2$	70	$5 \times 2$

<sup>*a*</sup> Frequencies and intensities are in cm<sup>-1</sup> and km mol<sup>-1</sup>. Frequencies and intensities computed with B3LYP and BPW91/6-311+G(3df) in the harmonic approximation using the SDD core potential and basis set for metal atoms. <sup>*b*</sup> The mode symmetry notations are based on the  $C_{3v}$ structure. Using B3LYP the degenerate modes were split 3 to 8 cm<sup>-1</sup>, and average values are reported here, but BPW91 gave degenerate modes and identical bond lengths. <sup>*c*</sup> Observed in an argon matrix. Argon matrix site absorptions at 566.9 and 532.0 cm<sup>-1</sup>.

than those for BPW91, which is the expected relationship for these calculations.<sup>24,25</sup> Notice also that the structural parameters are also nearly the same for the two functionals, which substantiates our modeling of this triplet ground state molecule. It is interesting to note that four of these calculations converged very close to  $C_{3v}$  symmetry and the other two converged to  $C_{3v}$  symmetry (Table 4).

#### Identification of the $E \div ThF_3$ molecules

Reactions of Th atoms with NF<sub>3</sub> gave new 575.5, 525.2, and 430.0 cm<sup>-1</sup> product absorptions, which are compared in Table 1 with frequencies calculated for the lowest energy product molecule. The most intense band at 525.5 cm<sup>-1</sup> is just above the strongest band at 521.3 cm<sup>-1</sup> from the CHF<sub>3</sub> reaction with Th, which was assigned to the antisymmetric degenerate Th-F stretching mode of HC÷ThF<sub>3</sub> calculated at 526 cm<sup>-1</sup> using the same methods.<sup>14</sup> Likewise, the weaker 575.5 cm<sup>-1</sup> band is also slightly higher than the weaker 565.4 cm<sup>-1</sup> band computed at 568 cm<sup>-1</sup> for the symmetric Th-F stretching mode of the carbon species. This favorable comparison with observed and calculated Th-F stretching frequencies for the isoelectronic HC÷ThF<sub>3</sub> molecule, and agreement of the observed frequencies within 3-8 cm<sup>-1</sup> with those computed for  $N \div ThF_3$  (Table 1) substantiates this identification and assignments. Only the strongest band was observed, at 536.1 cm<sup>-1</sup>, in the neon matrix experiment, and the 11 blue shift is reasonable for this guest molecule.26 The weakest band in solid argon at 430.0 cm<sup>-1</sup> band is lower than the 502.1 cm<sup>-1</sup> C-Th stretching mode of HC÷ThF<sub>3</sub> and also lower than the 454 cm<sup>-1</sup> computed value of the corresponding N-Th stretching mode, but close enough to support this assignment. The observation of this additional diagnostic frequency for the N÷ThF<sub>3</sub> molecule supports its identification.

The weaker nearby 565.0 and 531.0 absorptions give way on ultraviolet irradiation to the above bands assigned to the  $N \div ThF_3$  lowest energy reaction product from the Th metal atom reaction with NF<sub>3</sub>, and the latter bands are most likely due to a less stable argon matrix trapping site. This proposal is supported by similar observations in the analogous experiments with PF<sub>3</sub> and AsF<sub>3</sub>.

Parameter	$N \div ThF_3(B3)$	$N \div ThF_3(BP)$	$P \div ThF_3(B3)$	$P \div ThF_3(BP)$	$As \div ThF_3(B3)$	$As \div ThF_3(BP)$
$r(E \div Th)$	2.378	2.367	2.905	2.890	3.012	2.997
r(Th–F)	2.117/2.118	2.114/2.116	2.108/2.110	2.108	2.107/2.109	2.107
<(E-Th-F)	106.7/107.0	106.7/107.0	106.1/106.9	106.2	106.2/107.2	106.2
$q(\mathbf{E})^b$	-0.71	-0.66	-0.50	-0.51	-0.27	-0.27
$q(Th)^b$	2.65	2.45	2.43	2.27	2.20	2.04
$q(\mathbf{F})^{b}$	-0.65	-0.60	-0.64	-0.59	-0.64	-0.59
$s(E)^c$	1.901	1.888	1.933	1.909	1.976	1.983
$s(\mathbf{M})^c$	0.075	0.085	0.051	0.076	0.003	-0.005
$s(\mathbf{F})^c$	0.008	0.009	0.005	0.005	0.007	0.007
$M^d$	1.23	1.18	1.27	1.31	1.15	1.21
$\Delta E^{e}$	340	334	169	193	215	222

**Table 4** Structural parameters and physical constants for triplet state pnictinidenes  $E \div ThF_3$  (E = N, P, As) in  $C_s$  or  $C_{3v}$  symmetry<sup>a</sup>

<sup>*a*</sup> Bond lengths and angles are in Å and degrees. All calculations performed at the B3LYP or BPW91//6-311+G(3df)//SDD level. <sup>*b*</sup> Mulliken atomic charges. <sup>*c*</sup> Mulliken atomic spin densities: value given for only one fluorine atom. <sup>*d*</sup> Molecular dipole moment in D. <sup>*c*</sup> Binding energy in kcal mol<sup>-1</sup> relative to Th + EF<sub>3</sub>.

Although the  $PF_3$  precursor is less reactive as attested by much weaker  $ThF_4$  absorptions, the major product absorption at 528.3 cm<sup>-1</sup> is stronger than the nitrogen counterpart. The stronger 528.3 and weaker 569.1 cm<sup>-1</sup> absorptions track together and increase at the expense of the 566.3 and 531.3 cm<sup>-1</sup> bands on photolysis, which decreases but does not destroy the second pair of bands. The assignment of these two pairs of bands to different matrix sites is also supported by the neon matrix spectra, also shown in Fig. 2, where the 567.9 and 539.8 cm<sup>-1</sup> bands in neon correspond to the 569.1 and 528.3 cm<sup>-1</sup> bands in solid argon, and the 524.6 and 566.5 cm<sup>-1</sup> shoulders in neon correspond to the 565.0 and 531.0 cm<sup>-1</sup> satellites in argon.

The symmetric and antisymmetric Th–F stretching modes for  $P \div ThF_3$  are predicted to be very close to those for  $N \div ThF_3$ , and the observed bands correlate very well (Tables 1 and 2). This correlation is even closer for the  $As \div ThF_3$  product where the observed and calculated bands for both density functionals (Table 3) are within 1 cm<sup>-1</sup> of those for the  $P \div ThF_3$  product. Thus, the closely related observed and computed Th–F stretching modes for the three thorium pnictinidene molecules substantiate our assignments and identifications of these novel species.

#### Structure and bonding in the thorium pnictinidenes

Structural parameters computed for the triplet state pnictinidenes  $E \div ThF_3$  given in Table 4 reveal a progressive increase in the E–Th bond length, but the Th–F bond lengths and E–Th–F angles are the same within the error of calculation. The molecules have essentially  $C_{3v}$  symmetry structures, which are illustrated in Fig. 4.

The Mulliken atomic spin densities add to 2.00, which characterizes these triplet state  $E \div ThF_3$  pnictinidene species. Notice that the spin densities on N, P, and As increase from about 1.89 to 1.92 to 1.98, respectively, as progressively less spin is transferred to the Th centers from the more diffuse *n*p valence orbitals. Natural bond orbital analysis<sup>15,20</sup> performed for this series reveal  $\pi_{\alpha}$ molecular orbitals populated completely from the non-metal with very little Th 6d overlap, which are shown in Fig. 5. The analogous group 4 early transition metal pnictinidenes  $E \div MF_3$  exhibit more metal *n*d valence orbital involvement in the weak  $\pi$  bonding



**Fig. 4** Structures calculated for the thorium trifluoride pnictinidenes using B3LYP/6-311+G(3df)/SDD methods.

interaction.<sup>8</sup> In addition the  $\pi_{\alpha}$  molecular orbitals for HC ÷ ThF<sub>3</sub> have a 12% contribution from C, and the  $\pi_{\alpha}$  molecular orbital plot



electron density for bonding with N in the trihydride species, which has a much shorter 2.006 Å computed N–Th bond length and  $C_s$ symmetry.<sup>28</sup> This is demonstrated by the Mulliken atomic spin densities [1.28, 0.20, 0.22, 0.22, 0.08], which show considerable delocalization of the two unpaired electrons. The non-degenerate  $\pi_{\alpha}$  molecular orbitals are accordingly 88% N (100% p) and 12% Th (5% p, 47% d, 48% f), and 80% N (21% s, 79% p) and 20% Th (66% d, 30% f). In contrast there is no Th contribution to the  $\pi_{\alpha}$ molecular orbitals in N÷ThF<sub>3</sub>.

# Conclusions

The group 15 trifluoride molecules NF<sub>3</sub>, PF<sub>3</sub>, or AsF<sub>3</sub> were reacted with laser-ablated Th atoms to produce the actinide triplet state pnictinidene N $\div$ ThF<sub>3</sub>, P $\div$ ThF<sub>3</sub>, or As $\div$ ThF<sub>3</sub> molecules, as identified by their matrix infrared spectra and comparison to theoretically predicted vibrations. Density functional theory calculations using B3LYP and BPW91 functionals converge approximately to  $C_{3v}$  symmetry structures with relatively long terminal group 15 bonds to Th for these lowest energy triplet state products. Spin density calculations show that the two unpaired electrons are mostly localized in nitrogen 2p, phosphorus 3p, or arsenic 4p orbitals and thorium has a small spin density. The weak degenerate  $\pi_{\alpha}$  molecular orbitals are populated entirely from the terminal N, P, or As atoms based on DFT natural bond orbital analysis. In contrast, the related HC÷ThF<sub>3</sub> molecule<sup>28</sup> exhibits slightly more interaction through degenerate  $\pi_{\alpha}$  molecular orbitals with 81% C and 19% Th character and the analogous U reaction with AsF<sub>3</sub> produced the terminal arsenide As $\equiv$ UF<sub>3</sub> with a weak triple bond.27

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the pnictinidene series  $N \div ThF_3$ ,  $P \div ThF_3$ , and  $As \div ThF_3$  plotted with an iso-electron density of 0.02 e au<sup>-3</sup> using B3LYP/6-311+G(2d)/SDD methods.

(Fig. 10 in ref. 14) reveals more interaction with the Th metal center than found here for  $N\div ThF_3.$ 

In contrast, the analogous U reaction with AsF<sub>3</sub> produced the terminal arsenide As=UF<sub>3</sub> with a weak triple bond of computed length 2.544 Å, but clearly weaker than those formed in P=UF<sub>3</sub> and N=UF<sub>3</sub>.<sup>11,27</sup> Hence,  $\pi$  bonding with the *n*p valence orbitals of N, P, and As appears to be more favorable with the more compact 5f valence orbitals of U than with those of Th.

The bonding in the higher energy N÷ThH<sub>3</sub> molecule provides a very interesting comparison to that in N÷ThF<sub>3</sub>. As might be expected, the Mulliken charges are quite different [–0.74, 1.83, –0.36 × 3] in the trihydride so Th retains more of its valence

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