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Matrix Infrared Spectra and Electronic Structure Calculations of the First Actinide Borylene: $FB{=}ThF_2$

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Long abstract

Laser-ablated Th atoms react with BF_3 during condensation in excess argon at 6 K to form the first actinide borylene ($FB{=}ThF_2$) and actinide - boron multiple bond. Three new product absorptions in the B-F and Th-F stretching regions of matrix infrared spectra are assigned to $FB{=}ThF_2$ from comparison to theoretically predicted vibrational frequencies, and infrared spectra of ThF_4 and the group 4 $FB{=}MF_2$ molecules. CASSCF/CASPT2 and density functional theory calculations converge to a nonplanar C_s structure for the lowest energy singlet state reaction product. CASSCF/CASPT2 calculations describe an effective Th=B bond order of 1.91, which may be compared to effective bond orders of 1.81, 1.86, and 1.90, respectively, for the double bonds in the analogous Ti, Zr, and Hf borylenes ($FB{=}MF_2$).

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Table 1: Observed and Calculated Fundamental Frequencies for the Thorium Borylene Complex FB=ThF_2 in the Ground ^{1}A' Electronic State with C_s Structure[a]

Approx. mode Description	$F^{11}B=ThF_2$						
	obs	calc(CA)	int	calc(B3)	int	calc(BP)	int
B-F str, a'	1276	1324	1300	1333	963	1290	877
Th-F str, a'	539	553	77	542	51	546	51
Th-F str, a"	523	533	254	530	196	534	172
Th-B str, a'		293	31	311	28	306	24
ThBF def, a"		272	8	299	3	294	8
ThBF def, a"		239	3	261	3	246	5
ThF_2 bend, a'		97	11	107	17	92	14
FBThF def, a"		76	3	89	1	75	1
BThF_2 def, a"		13	27	85	10	69	6

[a]Frequencies and intensities are in cm^{-1} and km/mol. Observed in an argon matrix. Frequencies and intensities calculated with CASPT2/VTZP, B3LYP or BPW91/6-311+G(3df)/SDD in the harmonic approximation and denoted (CA), (B3), or (BP), respectively. Mode symmetry notations are based on the C_s structure.