the gauche outer (relative to the methyl groups) conformer will be the most stable form since the methyl groups are again in the trans position, the lone pairs on phosphorus are in a gauche relationship, and the number of gauche interactions between lone pairs and the polar P–C bonds is at a maximum.

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Registry No. $CH_3HPPHCH_3$, 53684-00-7.

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Ultraviolet Photoionization Spectra of the Valence Shell of (Difluorodithiophosphato)metal Complexes

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The He I photoelectron spectra of HS_2PF_2, $M^{II}(S_2PF_2)_2$ (M^{II} = Mn, Co, Ni, Zn), and $Cr(S_2PF_2)_3$ are reported. Absence of interfering ionization bands by substituent groups outside the chelate rings allows correlation of all relevant PE bands throughout the series and identification, besides d-ionization bands in the case of the Mn(II), Cr(III), Co(II), and Ni(II) complexes, of a series of six main bands, corresponding to all p-based σ and π molecular orbitals of the metal chelate rings.

Metal complexes of the ligand $F_2PS_2^-$, discovered and extensively investigated by Muetterties and co-workers[1,2] as well as by other authors,[3,4] appear particularly suitable for the investigation of their electronic structure by UPS (photoelectron spectroscopy with far-ultraviolet excitation) not only because of their high volatility but also because of the simplicity of their molecular structure, since the substituent groups outside the chelate ring do not exhibit low-energy ionization processes and hence do not interfere with the spectral PE patterns of the chelate ring orbitals. The UPS spectra of Cr(III), Mn(II), Co(II), Ni(II), and Zn(II) difluorodithiophosphates are indeed rich in well-resolved bands so that extensive empirical correlations are possible; we propose an assignment which accounts for all σ and π orbitals in the metal chelate rings, except those based mainly on atomic s-valence orbitals. Considerable insight into the electronic structure of the complexes can thus be gained, the partly filled d shell constituting the levels of highest orbital energy (except for the Zn(II) compound), followed by the ligand orbitals of coordinative π character, whose energies are quantitatively identified, and by the σ_{MS} and σ_{PS} orbitals. A comparison along the investigated series yields evidence for the trend of falling d-orbital energy with increasing atomic number.

Experimental Section

HS_2PF_2, $Cr(S_2PF_2)_3$, $Mn(S_2PF_2)_2$, $Co(S_2PF_2)_2$, $Ni(S_2PF_2)_2$, and $Zn(S_2PF_2)_2$ were synthesized according to known literature methods[1,2] and the metal compounds purified by sublimation. UPS were taken on a Perkin-Elmer PS-18 instrument equipped with a He I source (21.22 eV) and calibrated by the argon 3p and xenon or iodine (in CH_3I) 5p doublets. The metal complexes were introduced into the spectrometer chamber as solid samples, and HS_2PF_2 was introduced as a volatile liquid sample. Particular care was required in handling $Co(S_2PF_2)_2$ because of easy oxidation and HS_2PF_2 because of its high reactivity leading to rapid attack of spectrometer walls and photomultiplier surfaces. Calculations on the free ligand were carried out by the CNDO/2 method.[5]

Results and Discussion

He I UPS spectra of the above mentioned compounds are reported in Figure 1 and Table I. Three regions of ionization energy can be identified, in order of increasing orbital energies.

Region i. Between ca. 16 and 20 eV IE, three band groups are observed at about 16.2, 17.8, and 19.0 eV and are related to σ and π ionization of fluorine-based orbitals. Such ionizations are observed in the same energy region for all P–F

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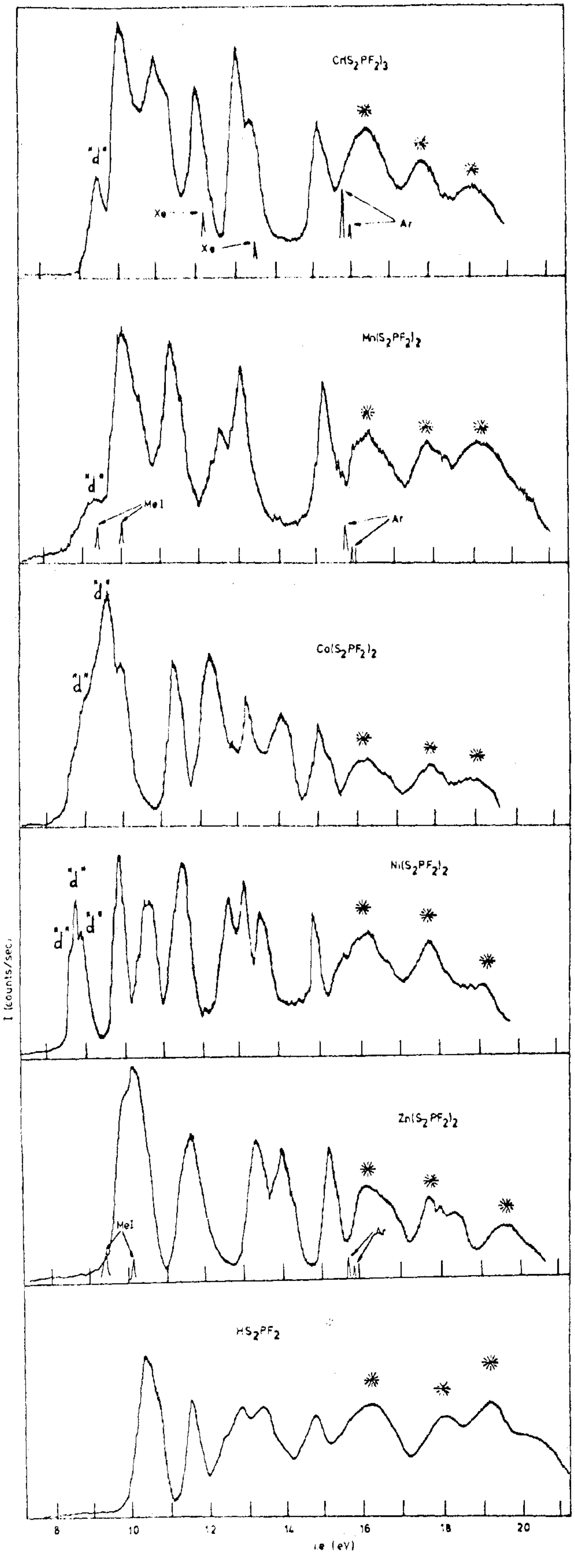


Figure 1. He I photoelectron spectra of $M(S_2PF_2)_n$ species ($M = Cr^{III}$, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, H). The asterisks mark the ionization peaks of F-based orbitals and "d" the metal-centered orbitals.

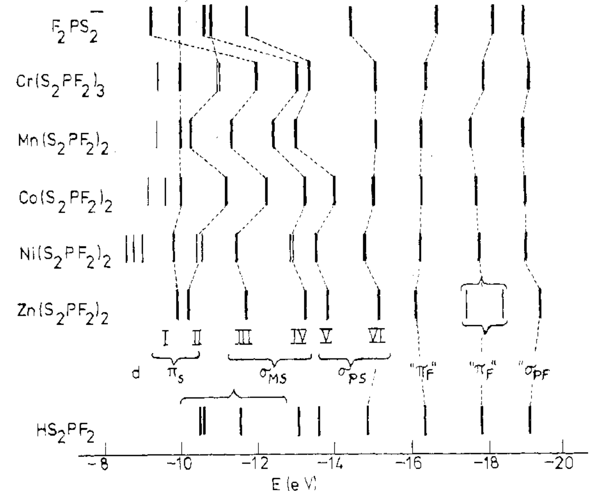
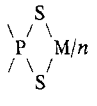


Figure 2. Correlation of ionization bands in the PE spectra of difluorodithiophosphate species (experimental data, except for $F_2PS_2^-$).

compounds of known PE spectrum, e.g., between 15.91 and 17.45 eV for PF_3,[6] 17.09 and 19.61 for OPF_3,[7] 16.51 and 18.65 for SPF_3.[8] The low symmetry of our difluorodithiophosphato complexes suggests four distinct π_F ionizations per ligand group, possibly grouped together two by two under the observed broad envelopes with maxima at ca. 16.2 and 17.8 eV. The third band, at about 19.0 eV, is related to σ_{PF} ionizations, which are predicted at orbital energies just below π_F, and actually observed at 19.5 (and 22.9) eV in PF_3,[6] 20.8 (and 23.4) in OPF_3,[7] and 20.05 in SPF_3,[8] although π_F and σ_{PF} character is probably mixed in all orbitals of this group, the latter being predominant in the lower levels. A slightly different profile of the second band of $Zn(S_2PF_2)_2$ is possibly related to d ionizations, which are reported between 17 and 19 eV in other Zn(II) compounds.[9,10]

Region ii. This extends between ca. 10 and 15 eV; the PE spectral patterns of the above complexes, although individually different, allow identification of a common sequence of six main bands I···VI, which we assign to the complete set of σ and π ligand-based orbitals of the coordination sphere. Such an assignment finds support in the fact that all valence orbitals (except those based on atomic s states) occur at higher energies than π_F and σ_{PF} orbitals in all P–F compounds of known PE spectrum[11,12] and in CNDO/2 calculations of the free $F_2PS_2^-$ and HS_2PF_2 ligands, placing six orbitals derived from three 3p orbitals of each sulfur atom above π_F and σ_{PF}, e.g., four n_S (two π_v, two π_h) lone pairs and two σ_{PS} bonding pairs in $F_2PS_2^-$ (see Table II).

By correlation with the MO sequence predicted for $F_2PS_2^-$ and by allowing for a shift to negative energies of the ligand orbitals which acquire metal–ligand σ character upon coordination (up to 2–3 eV for π_h), we propose to assign bands I (9.9–10.0 eV) and II (10.3–11.0) to both coordinative π_v electron pairs in each chelate ring



bands III (11.5–12.0) and IV (13.0–13.2) to σ_{MS} (from ligand π_h), and V (13.3–14.0) and VI (14.8–15.1) to both σ_{PS} bond orbitals, possibly mixed to some extent with σ_{MS} bonds.

Interligand interactions and the consequent lower symmetry splitting which might double the ionization bands corresponding to the orbital types I···VI are usually not evident except in isolated cases, e.g., band II of $Cr(S_2PF_2)_3$ at 10.93–11.03 eV and band IV of $Ni(S_2PF_2)_2$ at 12.84–13.04 eV.

Table I. He I PE Spectra[a] of Difluorodithiophosphates (Vertical Ionization Energies in eV)

Compd	d	I	II	III	IV	V	VI	π_F	π_F	σ_{PF}
HS_2PF_2		10.47	11.52	13.05	13.50		14.80	16.4	17.9	19.1
$Cr(S_2PF_2)_3$	9.41	10.02	10.93 11.03 sh	11.98	13.04	13.34	15.10	16.40 b	17.80 b	19.1 b
$Mn(S_2PF_2)_2$	9.38	10.08 b	11.20 11.50		12.44	13.00	15.14	16.22	17.55	19.0
$Co(S_2PF_2)_2$	9.18 sh 9.62	9.98	11.16	12.3	13.21	13.90	15.02	16.0 b	17.7 b	19.1 b
$Ni(S_2PF_2)_2$	8.62 sh 8.76 8.94 sh	9.84	10.45 10.58	11.44	12.84 13.04	13.47	14.76	16.17 b	17.85 b	18.95 b
$Zn(S_2PF_2)_2$		10.12	10.34	11.70	13.14	13.74	15.15	16.10 b	17.45 18.44	19.35

[a] Key: b = broad, sh = shoulder.

Table II. Difluorodithiophosphate Ligand: Experimental He I PE Ionization Data and CNDO/2 Calculated Orbital Energies (in eV)

HS_2PF_2			$[S_2PF_2]^-$	
Exptl	Calcd	Main eigenvectors	Calcd	Main eigen-vectors
10.47	−11.71	$n_S(\overset{+}{P}-S^-)$	−4.61	n_S, π_h(as)
	−12.17		−5.56	n_S, π_v(as)
11.52	−14.14	$\sigma(\overset{+}{P}-S^-)$	−6.14	n_S, π_h(s)
13.05	−15.14	$n_S(PSH)^a$	−6.29	n_S, π_v(s)
13.50	−16.81	PSH^b	−7.25	σ_{PS}(as)
14.80	−18.70	$\sigma_{SH}{}^c$ $(+\sigma_{P-SH})$	−10.06	σ_{PS}(s)
16.4	−19.03	π_F	−12.18	π_F
17.9	−20.11		−13.71	
19.1	−20.14		−13.80	
(20.4)	−21.98		−14.28	
	−22.23	σ_{PF}	−15.18	σ_{PF}
	−23.12		−16.10	

[a] Cf. 10.48 eV in H_2S.[19] [b] In-plane p_S orbital bisecting the PSH angle, with partial $\sigma_{PS} + \sigma_{SH}$ character; cf. 13.25 eV in H_2S.[19] [c] Cf. 15.35 eV in H_2S.[19]

The above assignment represents a rather unique case of identification of all valence orbitals of the coordination sphere of a metal chelate in its PE spectrum, made possible by the lack of interfering σ_{CH} and σ_{CC} ionizations, which obscure a large part of region ii in the PE spectra of other metal chelates containing organic ligands.

Region iii. The remaining bands at lower IE are assigned, both by exclusion criteria and by comparison with other metal complexes,[13-15] to d-orbital ionizations: the small band at 9.41 eV to d^3 in the Cr(III) complex, at 9.38 to high-spin d^5 in the Mn(II) complex, the broad structured band between ca. 8 and 10 eV to the tetrahedral d^7 system of $Co(S_2PF_2)_2$ (for which the overall splitting is likely to be <1 eV), and the band around 8.6–9.0 eV in the spectrum of $Ni(S_2PF_2)_2$ to the d^8 configuration of Ni(II) in square-planar environment, for which four filled orbitals, possibly grouped into two or three bands, are expected. The broad band at 8.6–9.0 eV could be due to the two highest filled d orbitals, the two lowest ones being masked under the ligand band at ca. 9.8 eV, but we prefer to regard all four d orbitals as present under the complex band contour peaked at 8.76 eV. Even if absorption spectroscopic data suggest[16] an overall splitting of the filled d orbitals >1 eV, deviations from Koopmans' behavior may well decrease such splitting to a few tenths of an electronvolt, as already observed in the PE spectra of other $[NiS_4]$ chromophores.[14,15] We mentioned already the possible occurrence of d ionizations in region i for $Zn(S_2PF_2)_2$.

On comparing our results on difluorodithiophosphates with the PE spectra of the analogous *O,O′*-diethyldithiophosphato (dtp) complexes reported recently,[17,18] a gross similarity of PE spectral patterns is evident, at least for the peaks at lower IE (up to ca. 11 eV, before ionization of n_O in the alkoxy groups) and apart from a parallel shift of 1–2 eV related to the inductive effect of fluorine atoms. Thus, the d ionizations of $Cr(S_2PF_2)_3$ at 9.41 eV and of $Ni(S_2PF_2)_2$ around 8.76 eV clearly correlate with the bands at 7.56 eV in $Cr(dtp)_3$ and 7.40 eV in $Ni(dtp)_2$;[17,18] a sequence of at least three main bands at about 8.4–9.0, 9.2–10.0, and 10.1–10.6 eV in $M(dtp)_n$ matches the first three ligand-based ionizations of $M(S_2PF_2)_n$, I at 9.9–10.1 eV, II at 10.5–11.1 eV, and III at 11.5–12 eV, and could be correspondingly assigned as the two coordinative π plus the higher σ_{MS} bond in each metal chelate ring. We agree with Maier and Sweigart[18] in assigning the band(s) between ca. 10.5 and 11.4 eV to the n_O ionizations in the $-OC_2H_5$ groups, while no further comparison with $M(S_2PF_2)_n$ is possible at IE > 12 eV, where σ_{CH} and σ_{CC} ionizations occur in the PE spectra of $M(dtp)_n$.

The amount of the parallel shift of IE values on going from dtp^- to $F_2PS_2{}^-$ compounds is metal dependent, being about 1.7 eV for Cr(III), 1.4 eV for Ni(II), and 1.1 eV for Zn(II) complexes, in line with the falling trend of d-orbital energies with increasing atomic number, i.e., with increasing difficulty for electronegative ligands to attract electronic charge from the central transition-metal ions. In the above correlations, we do not agree with the assignment of Maier and Sweigart,[18] who identify the band at 8.37 eV of $Ni(dtp)_2$ as a second d band and the highest π coordinative level at 9.2 eV instead of 8.37 eV; although as attractive as this assignment appears (it would in fact imply negligible energy shift of coordinative π orbitals between Hdtp and $M(dtp)_n$ and account for a d splitting compatible with absorption spectroscopic data[16]), it is contrasted by the fact that the band at 8.37 eV (8.45 in ref 17) occurs almost unchanged at 8.44 eV also in $Cr(dtp)_3$,[17] where it cannot be a d ionization.

Registry No. HS_2PF_2, 20773-09-5; $Cr(S_2PF_2)_3$(complex), 20728-62-5; $Cr(S_2PF_2)_3$(salt), 20046-81-5; $Mn(S_2PF_2)_2$(complex), 20728-55-6; $Mn(S_2PF_2)_2$(salt), 20448-07-1; $Co(S_2PF_2)_2$(complex), 20728-56-7; $Co(S_2PF_2)_2$(salt), 20046-75-7; $Ni(S_2PF_2)_2$(complex), 20728-57-8; $Ni(S_2PF_2)_2$(salt), 20046-76-8; $Zn(S_2PF_2)_2$(complex), 20728-59-0; $Zn(S_2PF_2)_2$(salt), 20046-78-0.

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Pulse-Radiolysis Studies of Americium Ions in Aqueous Perchlorate Media[1]

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The streak-camera technique was used to characterize the transient absorption spectra of Am(II) and Am(IV) in perchlorate media: λ_{max}(Am(II)) 312 nm, λ_{max}(Am(IV)) 320–340 nm. Second-order rate constants (M^{-1} s^{-1}) were measured for the following reactions: Am(III) + e_{aq}^-, (1.55 ± 0.04) × 10^8; Am(III) + OH, (4.1 ± 0.4) × 10^8; Am(IV) + Am(IV), (5 ± 1) × 10^6; Am(V) + e_{aq}^-, (3.18 ± 0.08) × 10^{10}, pH 6.0; Am(VI) + e_{aq}^-, (3.9 ± 0.9) × 10^{10}, pH 6.0.

Introduction

The chemistry of Am ions in aqueous perchloric acid media has been concerned with the 3+, 5+, and 6+ oxidation states where the species are the hydrated cations Am^{3+}, AmO_2^+, and AmO_2^{2+}. Evidence for the existence of the 4+ ions has been previously obtained only in strongly complexing media such as concentrated fluoride or phosphate solutions and Am^{2+} was identified in CaF_2 crystals.[2] The characterization of the oxidation–reduction patterns of Am(III), -(V), and -(VI) is hampered by the intense α-particle self-iirradiation that occurs in aqueous solutions. This explains, in part, the fact that quantitative data are available for only a limited number of oxidation–reduction reactions of americium ions.[3]

The primary considerations that motivated the present investigation were to explore the dynamic redox reactivity patterns of Am(III), -(V), and -(VI) with the reductant e_{aq}^- and the oxidizing radical OH when the latter are generated by pulse-radiolysis techniques and to characterize the Am(II) and Am(IV) ions produced in perchlorate media.[4]

Experimental Section

The lithium hydroxide, perchloric acid, and *tert*-butyl alcohol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The ^{243}Am was purified by a solvent extraction procedure[5] followed by precipitation of the americium(III) hydroxide which was washed, fumed to dryness with HNO_3–$HClO_4$ several times, and finally dissolved in 0.1 M $HClO_4$. Stock solutions of Am(III) were freshly prepared immediately prior to the pulse-radiolysis studies (after hydroxide precipitation and washing with triply distilled water until the supernatant was at a pH 7–8) and standardized spectrophotometrically at 503 nm (ϵ 450 ± 4). Am(V) and Am(VI) solutions were also prepared immediately prior to the pulse-radiolysis studies from the solid carbonate and carbonate solutions,[6] respectively, and standardized spectrophotometrically at 718 nm ($\epsilon_{Am(V)}$ 66 ± 1) L mol^{-1} cm^{-1} and 996 nm ($\epsilon_{Am(VI)}$ 107 ± 2) L mol^{-1} cm^{-1}.

The gas-saturating and cell-filling device has been previously described.[7] Spectra of the transient species produced by single electron pulses were obtained using a streak camera–TV scanning method described in a previous publication.[8] The irradiation procedure and dose measurements have been described.[9] The rate data were obtained by photomultiplier techniques where the output was stored in a Biomation Transient Recorder which in turn was interfaced with a Xerox Sigma 5 computer.

Table I. Apparent First-Order Rate Constants for the Reactions of e_{aq}^- and OH with Am(III) in Aqueous Perchlorate Media[a]

Eq 2 (e_{aq}^-)[b]		Eq 4 (OH)[c]	
[Am(III)], mM	$10^{-5}k_1'$ s^{-1}	[Am(III)], mM	$10^{-5}k_2'$ s^{-1}
7.90 × 10^{-2}	1.32 ± 0.02	0.733	4.88 ± 0.07
7.90 × 10^{-2}	1.32 ± 0.01	0.733	4.17 ± 0.04
0.158	1.35 ± 0.02	1.42	9.52 ± 0.09
0.158	1.43 ± 0.02	2.86	13.4 ± 0.1
0.316	1.65 ± 0.02	2.86	13.3 ± 0.1
0.316	1.70 ± 0.02	5.69	24.8 ± 0.3
0.632	2.18 ± 0.02	8.22	31.5 ± 0.5
0.632	2.10 ± 0.02		
1.24	3.10 ± 0.02		
1.24	3.04 ± 0.02		

[a] $T = 23 \pm 2$ °C, $\mu = 0.11$ M ($LiClO_4$). Uncertainties are standard deviations based on external consistency. [b] λ 650 nm, pH 5.8, He-saturated solutions 0.1 M in *tert*-butyl alcohol. [c] λ 320 nm, pH 5.1, N_2O-saturated solutions. Initial [OH] ≈50 μM.

The functional forms used were the standard integrated expressions for first- or second-order processes. The statistical adjustment[10] of the unweighted data in these forms used nonlinear least-squares programs (typically 300 data points per determination) with the three adjustable parameters A_0, A_∞, and k. A_0 and A_∞ are the absorptivities at time zero and at completion of the reaction, respectively, and k is either the apparent first-order rate constant or the second-order rate parameter/(molar absorptivity × path length). In all cases reported these three parameters provided an adequate description of the data. Standard deviations of the rate parameters quoted in the text were calculated on the basis of external consistency.

Results and Discussion

Spectra of Am(II) and Am(IV). The streak-camera method was used to observe the transient absorption spectrum that is identified as characteristic of the aquo ion Am(II). Am(II) was prepared by the reaction of Am(III) with e_{aq}^- and the spectrum is presented in Figure 1. The maximum at 312 nm is in a region that was not accessible to the investigators[11] who reported the spectrum of Am(II) in a CaF_2 crystal, a fact which precludes comparison between the solution and solid-state observations.

The transient absorption spectra identified as characteristic of Am(IV) were observed for the products of the reactions e_{aq}^- + Am(V) and OH + Am(III). The spectrum presented in Figure 2 for the latter reaction shows one broad band with a maximum between 320 and 340 nm.[12] The spectrum of the transient formed from the former reaction is similar to that displayed in Figure 2. The previous spectrophotometric studies of AmF_4 (solid) indicated a strong absorptivity below 350 nm[13] but the near-UV region was not accessible for detailed examination in that study.

Dynamic Studies. Reactions of Am(III). The data presented in Table I summarize the results obtained in the kinetic studies of the reactions of Am(III) with the hydrated electron and

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