Figure 4 the effect of varying the in-plane bond angles is shown. For $\varphi = 0°$ the bond angles are 90° and the g values have the required tetragonal symmetry; setting $\varphi = 1°$, i.e., the bond angles to 89 and 91°, can cause a splitting of $g_\perp$ of the order of 1.4.

The calculated g values are independent of the value of e_π^{Cl}, provided that relation 7 is used, since Δ_{pyz} remains constant. When e_π^{Cl} is set to 0, the value of e_σ^{Cl} is rather small, but it is expected to increase if e_π^{Cl} is given negative values. There is one point which is worth being considered. Assuming nonlinear ligation of the equatorial ligands as we have done implies that the usual relations for tetragonal complexes are no longer valid. In particular it is not true that $Dq^{ax} = Dq - {}^7/_4 Dt$. As a matter of fact the Dq of chlorine ($Dq = {}^3/_{10} e_\sigma - {}^4/_{10} e_\pi$) turns out to be extremely small from our calculated values. It is 400 when $e_\pi^{Cl} = 0$ and becomes smaller as it increases.

If the values of the parameters used for $Co(pyz)_4Cl_2$ are used for $Co(py)_4Cl_2$, only setting $e_{\pi\parallel}^{py} = e_{\pi\perp}^{py} = {}^1/_2 e_\pi^{pyz}$, a reasonable fit of the g values is found as shown in Table III. The agreement with the electronic transitions can be considered as fair, since they are more poorly resolved than those of $Co(pyz)_4Cl_2$. The value of Δ_{py} thus calculated is -250 cm^{-1}, which compares well with the value reported by Gerloch for the interpretation of the magnetic anisotropy data.[8] He actually used somewhat different values for e_σ^{py} and e_σ^{Cl}. Although they can change the energies of the electronic transitions a little, they do not influence the g values.

The present data do not allow us to obtain absolute values of e_π^{py}, e_π^{pyz}, and e_π^{Cl}; however it seems reasonable to use small values for all of these parameters, in accord with previous findings by Horrocks[6] and Gerloch.[8]

Registry No. $Co(py)_4Cl_2$, 14077-25-9; $Co(pyz)_4Cl_2$, 72843-09-5.

Contribution from the Materials and Molecular Research Division,
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Quasi-Relativistic SCF Xα Study of Octahedral 5f^1 Complexes[1]

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Quasi-relativistic SCF Xα calculations have been carried out for the octahedral 5f^1 complexes $Pa^{IV}X_6^{2-}$, $U^VX_6^-$ (X = F, Cl, Br, I), and $Np^{VI}F_6$. The 5f → 5f excitation energies calculated by using the transition-state method agree well with the available absorption spectra. Ionic effects appear to dominate the trends observed in the f-orbital ligand field splitting.

Introduction

Although ab initio calculations of ML_N complexes have been carried out extensively for the situation in which M is a transition metal or main-group element,[2a] lanthanide and actinide complexes have been somewhat neglected. Such calculations are computationally difficult for traditional LCAO schemes, although the multiple scattering Xα (MSXα) method is capable of solving such a problem without undue cost, even when relativistic effects are included. The Xα method has been applied to the neutral species UF_5,[2b] UF_6,[2b-6] UCl_6,[7] NpF_6,[4,5] and PuF_6.[4,5] Considerable success was obtained in their agreement with photoelectron and absorption spectra.

In the present study, quasi-relativistic SCF Xα calculations were carried out on a series of 5f^1 complexes: PaX_6^{2-}, UX_6^- (X = F, Cl, Br, I), and NpF_6. The study of such series has aided the interpretation of the electronic structure in terms of parameters commonly used in inorganic chemistry. In this case, the main object of study was the nature of the 5f ligand field splitting relative to the oxidation state of the metal ion and to the halide ion. Previously, only the relative extent of σ- and π-type ligand–f orbital interactions has been discussed, in terms of the semiempirical angular-overlap model.[8]

As a test of the SCF Xα calculations, 5f → 5f excitation energies were determined to compare with available experimental results.[9-11]

Computational Details

The calculations were performed by using a version of the MS Xα routine described by Slater,[12] modified, in the Dirac–Slater framework, to include relativistic effects. The Dirac–Slater MO model has previously been solved for a number of polyatomic systems by using the discrete variational method.[4] The computational effort necessary, however, is substantial but may be reduced considerably by constraining the potential to muffin-tin form. This allows the use of the efficient scattered-wave (SW) formalism either via Green's function technique[13] or by means of the elimination method.[14] The resulting secular equation for the orbital energies ϵ_i is of the same form as in the nonrelativistic SW formalism:[15]

$$\det|G_{pq}(\epsilon) - (\bar{\mu}_p{}^{-1}(\epsilon))\delta_{pq}| = 0$$

The propagators $G_{pq}(\epsilon)$ describe the scattering of the waves in the region of constant potential from sphere p to sphere q; they only depend

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(1) This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

(2) (a) W. G. Richards, P. R. Scott, E. A. Calbourn, and A. S. Marchington, "Bibliography of ab initio Molecular Wavefunctions—Supplement for 1976–1977", Oxford University Press, Oxford, 1978, and earlier publications in this series; (b) D. H. Maylotte, R. L. St. Peters, and R. P. Messmer, *Chem. Phys. Lett.*, **38**, 181 (1976).

(3) M. Boring and J. W. Moskowitz, *Chem. Phys. Lett.*, **38**, 185 (1976).

(4) D. D. Koelling, D. E. Ellis, and R. J. Bartlett, *J. Chem. Phys.*, **65**, 3331 (1976).

(5) M. Boring and H. G. Hecht, *J. Chem. Phys.*, **69**, 112 (1978).

(6) M. Boring and J. H. Wood, *J. Chem. Phys.*, **71**, 32 (1979).

(7) G. Thornton, N. Edelstein, N. Rösch, R. G. Egdell, and D. R. Woodwark, *J. Chem. Phys.*, **70**, 5218 (1979).

(8) K. D. Warren, *Inorg. Chem.*, **16**, 2008 (1977).

(9) D. Brown, P. Lidster, B. Wittaker, and N. Edelstein, *Inorg. Chem.*, **15**, 511 (1976).

(10) N. Edelstein, D. Brown, and B. Wittaker, *Inorg. Chem.*, **13**, 563 (1974).

(11) W. Wagner, N. Edelstein, B. Wittaker, and D. Brown, *Inorg. Chem.*, **16**, 1021 (1977).

(12) J. C. Slater, "The Self-Consistent Molecular Field for Molecules and Solids", McGraw-Hill, New York, 1974.

(13) C. Y. Yang and S. Rabii, *Phys. Rev. A*, **12**, 362 (1975); C. Y. Yang, *Chem. Phys. Lett.*, **41**, 578 (1976).

(14) R. Rosicky, P. Weinberger, and F. Mark, *J. Phys. B*, **9**, 2971 (1976).

(15) N. Rösch, *Electron Finite Infinite Syst., NATO Adv. Study Inst.*, 1 (1977).

0020-1669/80/1319-1304$01.00/0

Table I. Sphere Radii and Interatomic Distances Used in the MS Xα Calculations (au) and the Charge Found within Each Sphere for the Ground-State Complexes

	R_M	R_L	R_{OUT}	D_{ML}	Q_M	Q_{HAL}	Q_{INT}	Q_{OUT}
PaF_6^{2-}	3.212	1.3781	5.6767	2.274	89.582	7.843	9.148	1.208
$PaCl_6^{2-}$	3.212	2.2856	7.4920	2.754	89.351	16.039	8.482	0.925
$PaBr_6^{2-}$	3.212	2.5690	8.0586	2.904	89.414	34.031	8.480	0.891
PaI_6^{2-}	3.212	3.0280	8.9713	3.144	89.437	52.078	8.235	0.812
UF_6^-	2.789	1.3781	5.2666	3.888	90.879	7.803	8.927	1.197
UCl_6^-	2.789	2.2856	7.0816	4.796	89.879	16.018	8.147	0.859
UBr_6^-	2.789	2.5690	7.6484	5.079	89.982	34.014	8.093	0.815
UI_6^-	2.789	3.0280	8.5670	5.539	90.022	52.070	7.781	0.729
NpF_6	2.763	1.2322	4.9765	3.744	91.457	7.294	10.359	1.412

on the muffin-tin geometry. The scattering factors $\bar{\mu}_p(\epsilon)$ characterize the phase shift experienced by a wave on reflection at sphere p; it is a function of the logarithmic derivative of the large component of the wave function evaluated at the sphere boundary.[14,15]

In this study we use a nonperturbative self-consistent approximation to the SW treatment of the relativistic Xα model that should be well suited for MO calculations of very large molecules. The chemically relevant information is contained in the energies and wave functions of the valence-shell molecular orbitals. Core levels do not participate directly in the formation of chemical bonds and remain well localized in the vicinity of a nucleus. The SW model with its underlying muffin-tin geometry takes advantage of this fact in that it confines core levels to one atomic sphere, thereby treating them essentially as in atomic problems. For atoms, of course, the solution of the Dirac–Slater model is well established.[16]

In order to simplify the relativistic SW problems for valence shell MO's, we briefly analyze the magnitude of various relativistic effects for such orbitals. The spin–orbit splitting in molecules is usually smaller than in isolated atoms and at most ~1 eV for MO's with bonding energies less than ca. 20 eV. This has to be compared to errors in the orbital energies due to the muffin-tin form of the potential, which may be up to about the same size. The mass–velocity correction and the Darwin shift of MO energies may be 10 times larger. They affect the wave function wherever the quantity wherever

$$q = (1/2c^2)(\epsilon - V(\mathrm{r}))$$

is large, i.e., inside the atomic muffin-tin spheres. In the intersphere region where $|\epsilon - V(\mathrm{r})| \leq 4$ au these relativistic effects are completely negligible: $|q| \leq 10^{-4}$ ($c = 137$ au). The solution of the Dirac–Slater equation is therefore restricted to the interior of the atomic spheres.[16] The SW problem in the intersphere region is then identical with the nonrelativistic treatment except for the use of scattering factors $\bar{\mu}_p(\epsilon)$ calculated from the large component of the wave function inside the atomic spheres. A similar but more formal treatment, with applications mainly to atoms, has recently been presented by Wood and Boring.[17]

This approximation has the chemical appeal of reducing to the nonrelativistic treatment whenever the atomic number Z is small ($Z \leq 56$) or when c is made very large deliberately ($c \approx 10^6$ au). The same irreducible representations may be used as in the nonrelativistic case, and double groups necessary in the SW solution of the Dirac–Slater equation for molecules can be avoided. Spin–orbit splittings have to be estimated by using perturbation theory. The resulting errors will be tolerable since they are of the same size as those from the muffin-tin model.

The protactinium, uranium, and neptunium core electron charge densities were derived from relativistic calculations.[16] The interatomic distances used in the calculations (Table I) were taken from structural studies when available[18,19] or by reference to ionic radii tables.[20] The muffin-tin radii (Table I) were chosen as follows: An SCF Xα calculation of UF_6 was performed, and the sphere radii were adjusted to give the best overall agreement with the discrete variational Xα calculation of Koelling et al.[4] For this agreement the U and F spheres were overlapped. The U sphere radius was held constant at this value, while the other ligand radii were chosen to touch an imaginary sphere corresponding to a 10% reduction in the U sphere radius. The 10% overlap of the U sphere corresponds approximately to that present in the UF_6 calculation. The same ligand radii were then used for calculations on NpF_6 and PaX_6^{2-}. In these cases, the metal radii were chosen to give a 10% overlap. In all cases, the outer sphere was chosen to touch the ligand spheres, and for the anionic species a Watson sphere of the same radius was used. This carried a charge of 1+ for UX_6^- and 2+ for PaX_6^{2-}.

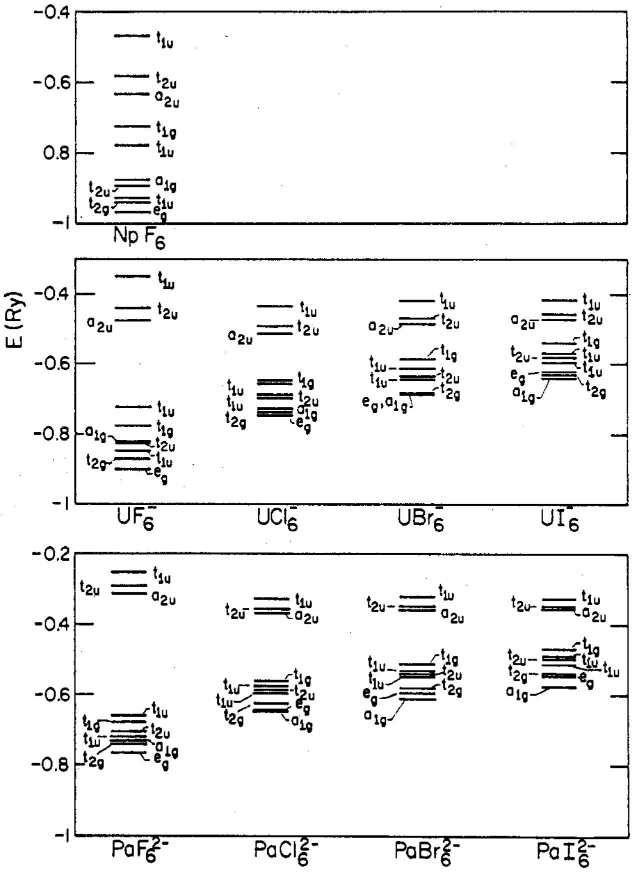

Figure 1. Calculated one-electron energies for the $5f^1$ hexahalide complexes.

The atomic exchange scaling parameters, α, were taken from values tabulated by Schwartz[21,22] or extrapolated from them.

$$\alpha_{\mathrm{Pa,U,Np}} = 0.69208,\ 0.6920,\ 0.6916$$

$$\alpha_{\mathrm{F,Cl,Br,I}} = 0.73732,\ 0.72325,\ 0.70606,\ 0.70008$$

Extramolecular and intersphere scaling parameters were obtained by averaging the atomic parameters. Core electron densities for Pa, U, and Np ([Xe]$4f^{14}$) were frozen at their atomic values as were the F([He]), Cl([Ne]), Br([Ar]), and I([Kr]) electron densities. All other electrons were considered fully in the SCF calculations, spin–orbit

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(16) D. A. Liberman, J. T. Waber, and D. T. Cromer, *Phys. Rev.* [*Sect.*] *A*, **137**, 27 (1965).
(17) J. H. Wood and A. M. Boring, *Phys. Rev. B*, **18**, 2701 (1978).
(18) D. Brown in "Comprehensive Inorganic Chemistry", Vol. 5, Pergamon Press, New York, 1973.
(19) A. Rosenzweig and D. T. Cromer, *Acta Crystallogr.*, **23**, 865 (1967).
(20) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 2446 (1972).
(21) K. Schwartz, *Phys. Rev.*, **85**, 2446 (1972).
(22) K. Schwartz, *Theor. Chim. Acta*, **34**, 225 (1974).

Table II. 5f → 5f Excitation Energies: Theoretical and Experimental[10-12] (cm^{-1})

	$a_{2u} \to t_{2u}$		$a_{2u} \to t_{1u}$	
	calcd	exptl	calcd	exptl
PaF_6^{2-}	2381	3074	6979	7576
$PaCl_6^{2-}$	1350	1634	4521	3507
$PaBr_6^{2-}$	1218	1707	4104	2975
PaI_6^{2-}	944	1546	3424	2378
UF_6^-	4148	4479	17130	11361
UCl_6^-	2294	2936	8658	6307
UBr_6^-	2008	2935	7725	5310
UI_6^-	1525		6277	
NpF_6	5662	5619	18676	23117

coupling being neglected. The Xα one-electron energies found in the calculations are shown in Figure 1, and the electron charge within each muffin-tin sphere is presented in Table I.

Discussion

An appropriate test for the calculations presented here is to compare the calculated 5f–5f excitation energies with corresponding absorption spectra. Table II shows this comparison and it can be seen that the agreement between theory and experiment is remarkably good. The excitation energies were calculated by using the transition-state procedure of Slater.[12]

The trend in the calculated ligand field splittings observed in Figure 1 follows that found experimentally and that expected from the spectrochemical series, i.e., $F^- > Cl^- > Br^- > I^-$. Also, the order $Np^{6+} > U^{5+} > Pa^{4+}$ expected on purely ionic grounds is observed. In the MS Xα scheme a charge fraction analysis of each of the orbitals can reveal the relative σ and π contributions in each of the spheres. Following the work of Rösch et al.,[23] the intersphere charge density is divided between the metal (1 part) and ligand spheres (6 parts) and the charge density in the outer sphere is given to the ligands. Table III shows the results of this charge fraction analysis for the antibonding[24] and bonding t_{1u} and t_{2u} orbitals and the nonbonding a_{2u} orbital that contains the f electron. Although the absolute numbers are probably not meaningful, the relative values should be qualitatively correct.

The following trends are apparent on comparing the relative ligand contribution to the antibonding orbitals or the metal contributions to the bonding orbitals. The fluoride complexes are the most ionic in each of the various ionic groups, and the ligand contribution increases as the halide ion becomes heavier. Within a particular halide-complex series, the heavier the metal ion (and the lesser the total ionic charge) the greater the ligand contribution. In particular, NpF_6 appears to be the most covalent complex in the entire hexahalide series.

Considering only the t_{1u} antibonding orbitals, the percentage of ligand σ bonding increases from 17.4% (UF_6^- and 7.8% (PaF_6^{2-}) to 26.6% (UI_6^-) and 12.7% (PaI_6^{2-}). The ligand π-bonding component in the t_{1u} antibonding orbital increases from 2.3% and 2.6% in UF_6^- and PaF_6^{2-} to 5.5% and 3.9% in UI_6^- and PaI_6^{2-}. For the antibonding t_{2u} orbital (where only π bonding with the f orbitals can occur), the ligand π bonding increases from 8.5% and 4.8% for UF_6^- and PaF_6^{2-} to 11.6% and 6.2% for UI_6^- and PaI_6^{2-}.

The increase in both σ and π bonding as the halide becomes heavier is substantial. However, it is small when compared with the dramatic *decrease* in the f-orbital splitting as the ligand is changed from F^- to I^- (see Table II). These results suggest that the f-orbital splittings of these hexahalide complexes are dominated by ionic effects with a lesser contribution from covalent bonding. It appears that the decrease in ionic effects due to changes in bond length outweighs the gain in covalent bonding on descending the halogen series.

Table III. Energies and Composition of the a_{2u}, t_{1u}, and t_{2u} "5f" Orbitals

molecule	orbital	energy, Ry	% metal		% ligand	
			f	p	σ	π
PaF_6^{2-}	a_{2u}	−0.3117	96.56			
	t_{1u}	−0.2483[a]	88.39[b]	1.27	7.76	2.58
		−0.6592	5.71	8.28	63.56	22.46
		−0.7170	10.78	0.11	21.54	67.56
	t_{2u}	−0.2900[a]	95.19			4.81
		−0.7045	7.22			92.78
$PaCl_6^{2-}$	a_{2u}	−0.3691	97.29			
	t_{1u}	−0.3285[a]	86.13	0.74	10.11	3.01
		−0.5754	10.72	4.64	81.94	2.71
		−0.5941	7.19	0.30	2.31	90.19
	t_{2u}	−0.3568[a]	94.68			5.33
		−0.5861	6.96			93.04
$PaBr_6^{2-}$	a_{2u}	−0.3570	97.16			
	t_{1u}	−0.3202[a]	84.69	0.67	11.26	3.38
		−0.5311	14.38	3.39	81.69	0.54
		−0.5493	3.94	1.96	1.05	93.05
	t_{2u}	−0.3459[a]	94.22			5.79
		−0.5393	7.26			92.74
PaI_6^{2-}	a_{2u}	−0.3551	97.28			
	t_{1u}	−0.3246[a]	82.89	0.55	12.66	3.89
		−0.4884	17.27	1.90	70.54	10.29
		−0.5107	0.22	4.78	13.21	81.80
	t_{2u}	−0.3465[a]	93.84			6.16
		−0.4959	7.31			92.69
UF_6^-	a_{2u}	−0.4740	96.28			
	t_{1u}	−0.3479[a]	77.93	2.40	17.42	2.25
		−0.7205	10.76	9.57	50.94	28.74
		−0.8452	15.92	10.17	22.84	61.06
	t_{2u}	−0.4363[a]	91.52			8.48
		−0.8221	10.27			89.73
UCl_6^-	a_{2u}	−0.5111	96.75			
	t_{1u}	−0.4333[a]	71.96	1.34	22.91	3.77
		−0.6561	16.37	4.48	64.04	5.11
		−0.6985	14.67	0.00	9.99	75.34
	t_{2u}	−0.4902[a]	89.83			10.17
		−0.6866	10.90			89.10
UBr_6^-	a_{2u}	−0.4857	96.64			
	t_{1u}	−0.4171[a]	69.96	1.13	24.53	4.38
		−0.6117	21.51	3.49	69.38	5.62
		−0.6444	11.52	0.16	2.72	85.60
	t_{2u}	−0.4676[a]	89.22			10.78
		−0.6329	11.29			88.71
UI_6^-	a_{2u}	−0.4706	96.61			
	t_{1u}	−0.4150[a]	67.01	0.86	26.64	5.47
		−0.5690	29.80	1.95	67.93	0.32
		−0.5953	5.06	1.26	2.14	91.53
	t_{2u}	−0.4568[a]	88.70			11.30
		−0.5815	11.48			88.52
NpF_6	a_{2u}	−0.6307	97.0			
	t_{1u}	−0.4631[a]	67.9	3.87	26.35	1.91
		−0.7753	14.09	8.97	37.48	39.45
		−0.9258	24.83	0.30	26.34	48.53
	t_{2u}	−0.5795[a]	86.45			13.55
		−0.8917	16.71			83.29

[a] Antibonding orbital. [b] Intersphere charge $^1/_7$ given to metal sphere, $^6/_7$ to ligands; within a ligand or metal orbital the intersphere charge is divided proportionately among the various components according to the percentage of charge density for each partial wave. The outer-sphere charge density is distributed only on the ligands in the same fashion.

Table IV. Gross Atomic Charges

	M	L		M	L
PaF_6^{2-}	0.11	−0.35	UCl_6^-	0.96	−0.33
$PaCl_6^{2-}$	0.44	−0.41	UBr_6^-	0.86	−0.31
$PaBr_6^{2-}$	0.38	−0.39	UI_6^-	0.87	−0.30
PaI_6^{2-}	0.39	−0.39	NpF_6	0.06	−0.01
UF_6^-	0.68	−0.28			

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(23) N. Rösch, V. H. Smith, Jr., and M. H. Whangbo, *Inorg. Chem.*, **15**, 1768 (1976).

(24) In the case of the antibonding orbitals, the analysis is of virtual charge.

Another measure of the covalent/ionic nature of the complexes can be found in the gross atomic charge assigned to the metal and ligand, as shown in Table IV. This is equivalent to a Mulliken population analysis in the LCAO scheme. The pattern obtained here is different from that discussed previously considering only the f orbitals. Clearly, NpF_6 is the most covalent, but PaF_6^{2-} appears more covalent than UF_6^-. However, if the bonding is mainly ionic, then these results are consistent; i.e., the greater the charge on the complex as a whole the smaller the charge on the central ion. Since the F^- ion is the smallest and least polarizable halide ion, an overall charge on the complex will result in more charge being placed on the central metal ion. There appears to be little difference for the other halide ions.

Summary

This paper has described a systematic study of the 5f ligand field splitting in the $5f^1$ complexes $Pa^{IV}X_6^{2-}$, $U^VX_6^-$ (X = F, Cl, Br, I), and $Np^{VI}F_6$. A quasi-relativistic MS Xα routine was used for this purpose. The trends observed in the f-orbital ligand field splitting appear to be principally ionic.

Registry No. PaF_6^{2-}, 49864-66-6; $PaCl_6^{2-}$, 44463-14-1; $PaBr_6^{2-}$, 44463-09-4; PaI_6^{2-}, 44463-23-2; UF_6^-, 73017-47-7; UCl_6^-, 44491-58-9; UBr_6^-, 44491-06-7; UI_6^-, 73002-73-0; NpF_6, 14521-05-2.

Contribution from the Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ Scotland,
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Electronic Structure of the Sulfur Nitrides. Ab Initio Calculations and Photoelectron Spectra

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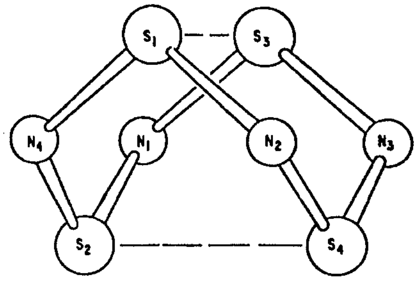
Ab initio molecular orbital calculations of better than double-ζ quality are reported for SN, S_2N_2, S_4N_4, and a number of open-shell cationic states; midbond functions (on all molecules) and polarization functions on S_2N_2 are included. The gas-phase UV–photoelectron spectra (PES) up to 25 eV have been investigated and assigned on the basis of the calculations and cross-section changes under He I/He II irradiation. The electronic structures of S_2N_2 and S_4N_4 were investigated by transformation of the wave functions to a localized bond basis. A significant amount of S–S bonding was calculated for S_4N_4 but no N–N bonding. Across ring bonding was absent from S_2N_2.

Introduction

The long-known series of sulfur nitrides $(NS)_x$, where x = 1–4, have been widely investigated[1] and contrast sharply with the corresponding series $(NO)_x$ with x = 1, 2, 3, and 4 where only the first is well-known. Particular impetus to the study of the NS series has been provided by the remarkable electronic properties of the chain-type metallic conductor $(SN)_x$.[2]

Tetrasulfur tetranitride, S_4N_4 (**1**), is perhaps the most well-known member of the series, the molecular structures being based on a square-planar array of nitrogen atoms inserted within a approximately tetrahedral quartet of bridging sulfur atoms.[3] The dimer, disulfur dinitride S_2N_2 (**2**), consists of alternating S and N atoms and is essentially square;[4] it is the usual precursor for polymeric $(SN)_x$.



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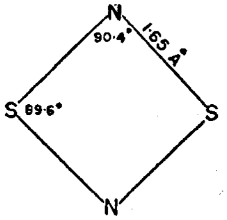

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In the present work we discuss the electronic structures of (a) S_2N_2 and (b) S_4N_4, both at their known crystal structure geometries,[3,4] and (c) SN, at the microwave geometry,[5] together with a number of open shell cationic states, for which the geometry is assumed to be the same as the ground state. The actual dimensions used were SN = 1.4957 Å, SN = 1.657 Å and SNS = 90.42° in S_2N_2, and SN = 1.616 Å and NSN = 104.5° in S_4N_4 (D_{2d}).

We assume that the molecular structures of the crystalline solids are still relevant to the gaseous S_2N_2 and S_4N_4 molecules; the similarity of the vibrational spectrum of S_2N_2 in the solid and gas phases supports this assumption. A number of previous electronic structure calculations have been reported for the present series of molecules: (a) for SN and/or SN^+ Xα[6] and ab initio (i) STO-3G,[7] (ii) extended basis,[8,9] and (iii) uhf;[10] (b) for S_2N_2 CNDO-2,[11,12] CNDO-S,[13] INDO (trip-

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(1) Banister, A. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1975**, *3*, 41.
(2) Greene, R. L; Street, G. B. *Chem. Phys. One Dimensional Met. Proc. NATO Adv. Study Inst.* **1976**, 1. Geserich, H. P.; Pintschovius, L. *Festkorperprobleme*, **1976**, *16*, 65.
(3) Sharma, B. D.; Donohue, J. *Acta Crystallogr.* **1963**, *16*, 891.
(4) (a) MacDiarmid, A. G.; Mikulski, C. M; Russo, P. J.; Saran, M. S.; Garito, A. F.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1975**, 476. (b) Mikulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358. (c) Cohen, M. J.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *Ibid.* **1976**, *98*, 3844.
(5) Zeeman, P. B. *Can J. Phys.* **1951**, *29*, 174.
(6) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039.
(7) Deutsch, P. W.; Curtiss, L. A. *Chem. Phys. Lett.* **1977**, *51*, 125.
(8) O'Hare, P. A. G. *J. Chem. Phys.* **1970**, *52*, 2992.
(9) Jafri, J. A.; Newton, M. D.; Pakkanen, T. A.; Whitten, J. L. *J. Chem. Phys.* **1977**, *66*, 5167.
(10) Török, F.; Pulay, P.; Szondy, T.; Nagy, P. *Acta Chim. Acad. Sci. Hung.* **1974**, *80*, 139.
(11) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1383. Adkins, R. R.; Dell, R.; Turner, A. G.; *J. Mol. Struct.* **1976**, *31*, 403.
(12) Kertesz, M.; Suhai, S.; Azman. A.; Kocjan, D.; Kiss, A. I. *Chem. Phys. Lett.* **1976**, *44*, 53.
(13) Salanek, W. R.; Lin, J. W-p.; Paton, A.; Duke, C. B.; Ceasar, G. P. *Phys. Rev. B.* **1976**, *13*, 4517.

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