Excited States and Positive Ions of SF_6

P. Jeffrey Hay

Contribution from the Theoretical Division, Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545. *Received July 19, 1976*

Abstract: The excited electronic states of SF_6 and the lowest states of SF_6^+ are investigated with ab initio calculations in an extended Gaussian basis. The ordering of the states of SF_6^+ as predicted by orbital energies of SF_6 or by SCF calculations on SF_6^+ differs from the ordering predicted by calculations which include electron correlation. The excited states of SF_6 are treated by improved virtual orbital (IVO) calculations where the excited state orbitals are determined in the field of the appropriate ion core. The lowest excited states correspond to excitations into the $6a_{1g}$ orbital, a valence-type orbital with considerable S–F antibonding character. Higher excited states involve excitations into diffuse Rydberg 4s, 4p, or 3d orbitals. The term values for states involving the $6a_{1g}$ orbital vary by as much as 13 000 cm^{-1} depending upon which orbital is excited, while the term values for true Rydberg states are not affected greatly by the nature of the ion core. Oscillator strengths for the dipole-allowed states are reported, and some excitations from core orbitals in x-ray absorption are investigated.

The SF_6 molecule has been studied by a variety of experimental techniques including UV and vacuum UV,[1-3] electron-impact,[4] photoelectron,[5,6] and x-ray spectroscopy.[7-9] The assignment of the lowest states of SF_6^+ has been controversial since four peaks are observed in the photoelectron spectrum in the region 15–20 eV but five electronic states are predicted to lie in this region. Theoretical interpretations have been based on orbital energies from SCF calculations[10,11] on SF_6, from many-body perturbation theory,[11] and from $X\alpha$-scattered wave calculations.[12] In the only ab initio treatment to date of the excited states of SF_6, Gianturco[13] employed a small Gaussian basis which would not have sufficient flexibility to treat any states involving diffuse Rydberg orbitals. Using theoretical estimates for the term values of Rydberg states, Robin[14] assigned many of the peaks in the UV and electron-impact spectra of SF_6.

In this study an extended Gaussian basis with added diffuse functions is used to calculate the excited states of SF_6. In the improved virtual orbital (IVO) method[15] each state is represented as a single electron in the field of a "frozen" ion core of particular symmetry. Although this simple approach neglects such effects as relaxation and electron correlation, the calculated results appear to be in good agreement with the experimental information and to be at variance with some of the earlier theoretical interpretations. The agreement between theory and experiment is aided by the customary procedure of correcting the calculated excitation energies by the difference between the Hartree–Fock and experimental ionization potentials. The interpretation of the SF_6^+ states themselves is based on the results of CI calculations using the generalized valence bond (GVB) orbitals of SF_6.[16]

Details of the Calculation

Positive Ions. Three different techniques were employed for the states of SF_6^+. The simplest method uses Koopmans' theorem to assign the IP as $-\epsilon_i$, where the orbital energies are taken from the Hartree–Fock calculation on SF_6. The (11s7p1d/9s5p) Gaussian basis contracted to [4s3p1d/3s2p] discussed in the preceding paper was used.[16] Self-consistent calculations were performed on the ion states in the same basis to assess the importance of orbital relaxation effects. For the degenerate states such as $^2T_{1u}$ arising from the $(t_{1u})^5$ configuration, the x, y, and z t_{1u} components were required to be spatially equivalent by the use of an average open-shell Hamiltonian. Allowing the t_{1uz} component to be nonequivalent in the configuration $(t_{1ux})^2(t_{1uy})^2(t_{1uz})^1$ resulted in an energy lowering of approximately 0.01 au (0.3 eV). The open-shell calculations allowed complete mixing of the open- and closed-shell orbitals of a given symmetry.

The GVB–CI calculations for SF_6^+ used the six-pair generalized valence bond (GVB) calculation of the neutral molecules as a starting point.[16] The GVB natural orbitals were transformed to octahedral symmetry functions, and the resulting 41 orbitals formed the basis set for the CI calculations. In terms of these orbitals the Hartree–Fock configuration is represented by $(4a_{1g})^2$ $(5a_{1g})^2$ $(3t_{1u})^6$ $(4t_{1u})^6$ $(5t_{1u})^6$ $(2e_g)^4$ $(3e_g)^4$ $(1t_{2g})^6$ $(1t_{1g})^6$ $(1t_{2u})^6$ $(6a_{1g})^0$ $(6t_{1u})^0$ $(4e_g)^0$. The 11 core orbitals not listed in this configuration describe the sulfur 1s, 2s, 2p and fluorine 1s electrons, and these orbitals were held doubly occupied in the CI calculations.

All single and double excitations relative to the reference configurations in the above space of orbitals were generated. The reference configuration consisted of the Hartree–Fock configuration for SF_6. For the SF_6^+ states the reference states comprised all configurations of a particular symmetry obtained by removing one electron from the Hartree–Fock configuration. Thus the three $^2T_{1u}$ reference states corresponded to the $(3t_{1u})$, $(4t_{1u})$, and $(5t_{1u})$ "hole" states of SF_6^+. The configurations were then screened by perturbation theory and ones with estimated energy contributions of 5×10^{-5} au were retained in the final variational CI. The number of final spin eigenfunctions in the CI calculations for SF_6 and SF_6^+ (and the total number of spin eigenfunctions before selection) are as follows: $^1A_{1g}$ 408 (1591); ^2E_g 1018 (7864); $^2T_{1u}$, $^2T_{2u}$ 2253 (14697); and $^2T_{1g}$, $^2T_{2g}$ 1883 (8913). More than one octahedral symmetry can occur in a particular calculation since the D_{2h} point group, the highest symmetry group containing only one-dimensional representations, was employed.

To assess the reliability of the selection procedure the SF_6 calculations were repeated using all 1591 spin functions without selecting. The resultant total energy was 0.12 eV lower (−994.1907 compared to −994.1862 au) than the energy obtained using 408 selected configurations. Based on other experience to date we would expect the *relative* energy differences for the IP's themselves should be at least as accurate as the 0.1 eV error in *absolute* energies introduced by the selection procedure.

Excited States. In order to describe excited states which involve diffuse orbitals an additional set of basis functions centered on the sulfur atom was added to the valence basis. This consisted of three s functions with Gaussian exponents of 0.024, 0.0076, and 0.0025, two sets of p functions with exponents 0.020 and 0.007, and a set of d functions with exponent 0.016. These should be appropriate for describing the 4s, 5s, 6s, 4p, 5p, and 3d Rydberg orbitals of sulfur. Most of the exponents were determined by optimizing the energy for the quintet configuration $(3s)^2 3p_x 3p_y 3p_z\ \phi$ of the sulfur atom, where ϕ represents the Rydberg orbital. The outermost s and

Table I. The Ionization Potentials for SF_6 from Previous Calculations

	Gianturco[a]	Roos[b]	von Niessen et al.[c]		
Orbital	$-\epsilon_i$	$-\epsilon_i$	$-\epsilon_i$	MBPT	Xα-SW[d]
$1t_{1g}$	14.75	18.2	19.18	16.71	15.88
$5t_{1u}$	16.36	19.0	19.95	17.68	16.76
$1t_{2u}$	15.93	19.4	20.41	17.91	16.84
$3e_g$	17.25	19.4	20.41	18.47	17.52
$1t_{2g}$	20.88	22.2	23.36	20.81	18.74
$4t_{1u}$	23.22	24.7	25.67	23.41	21.84
Total energy of SF_6, au					
	−990.1283	−992.9313	−993.7867		

[a] Reference 10a. [b] Reference 10b. [c] Reference 11. [d] Reference 12.

Table II. The Ionization Potentials of SF_6 from the Present Calculations

	Hartree-Fock			
Orbital	$-\epsilon_i$	SCF	GVB-CI	Exptl[a]
$1t_{1g}$	19.15	18.63	16.88	15.7
$5t_{1u}$	19.96	19.44	18.05	17.0
$1t_{2u}$	20.39	19.89	18.09	17.0
$3e_g$	20.39	19.65	18.98	18.6
$1t_{2g}$	23.29	22.83	20.95	19.8
$4t_{1u}$	25.64			22.9
Total energy of SF_6, au				
	−994.0287	−994.0287	−994.1862	

[a] References 5 and 6.

p exponents, however, were chosen arbitrarily.

In the improved virtual orbital (IVO) procedure for molecules the energy of a state arising from the excitation $\phi_k \rightarrow \phi_l$ is calculated by constructing the hamiltonian for orbital ϕ_l with the appropriate ion core obtained by removing orbital ϕ_k. Thus for a configuration $\phi_1{}^2 \ldots \phi_n{}^2\phi_k\phi_l$

$$H_{\mathrm{IVO}} = t + V_{\mathrm{N}} + \sum_{i=1}^{n} (2J_i - K_i) + J_k \pm K_k$$

where the plus and minus signs refer to singlet or triplet states, respectively. The coulomb and exchange operators are denoted by J and K. The excitation energies are then given by $\Delta E = \epsilon_l - \epsilon_k$, where the ϵ_l's are the eigenvalues of H_{IVO} obtained in the space orthogonal to the occupied orbitals. Since all the ion states of interest in SF_6 are degenerate, the hamiltonian is averaged over all components. The IVO hamiltonian then has the form

$$H_{\mathrm{IVO}} = t + V_{\mathrm{N}} + \sum_{i=1}^{n} 2J_i - K_i + \sum_{k=1}^{d} 2aJ_k - bK_k$$

where d is the degeneracy of the ion core. For triply degenerate T states of the ion one has $a = 5/3$ and $b = 1/3$ for singlet coupling with the virtual orbital and $a = 5/6$ and $b = 1$ for triplet coupling. For doubly degenerate E states $a = 3/4$ and $b = 0$ for singlet states and $a = 3/4$ and $b = 1$ for triplet states. The excitation energy $\Delta\epsilon(k \rightarrow l)$ is then given by

$$\Delta\epsilon(k \rightarrow l) = \epsilon_l - \epsilon_k$$

where ϵ_l is the orbital energy from the IVO calculation and ϵ_k is the orbital energy of the occupied orbital in the Hartree-Fock calculations.

This procedure yields excitation energies which are average of configurations for the singlet or triplet manifolds. Since most of the excited orbitals are quite diffuse the splitting within these multiplets is expected to be quite small (~0.05 eV). The only valence excited orbital, as will be shown, is a nondegenerate a_{1g} orbital with no multiplet structure.

In general one expects the IVO excitation energies to be in error by about the same error in the computed ionization potential for the ion core. For this reason the excitation energies are corrected by the difference between the Hartree-Fock and the experimental IP's. As will be discussed this can lead to difficulties when the assignment of the ion states is uncertain.

Transition Moments. Transition moments for the dipole-allowed transitions were computed rising the relation

$$\mu_{kl} = \langle k|r|l\rangle$$

where k and l refer to the orbitals involved in the $k \rightarrow l$ excitation. To obtain the overall transition moment between the many-electron wave functions the quantity μ_{kl} is multiplied by an appropriate factor related to the number of terms in the final state ${}^1T_{1u}$ wave function. (Excited orbitals from the $5t_{1u}$ excitation were used to calculate transition moments.) The initial state is the single-determinant ${}^1A_{1g}$ wave function

$$\Psi_0 = |\phi_1\bar{\phi}_1 \ldots \phi_k\bar{\phi}_k \ldots \phi_n\bar{\phi}_n| \tag{1}$$

In the final state if ϕ_k and ϕ_l correspond to a $t_{1u}(x) \rightarrow a_{1g}$ excitation one has

$$\Psi_f = 2^{-1/2}|\phi_1\bar{\phi}_1 \ldots (\phi_k\bar{\phi}_l + \phi_l\bar{\phi}_k) \ldots \phi_n\bar{\phi}_n| \tag{2}$$

and

$$\mu_{0f}{}^x = (2/2^{1/2})\langle t_{1u}(x)|x|a_{1g}\rangle = 2^{1/2}\mu_{kl} \tag{3}$$

For a $t_{1u} \rightarrow t_{2g}$ transition the quantity in parentheses in (2) becomes

$$t_{2g}(xy)t_{1u}(y) + \overline{t_{1u}}(y)\overline{t_{2g}}(xy) + t_{2g}(xz)\overline{t_{1u}}(z) + t_{1u}(z)\overline{t_{2g}}(xz)$$

and $\mu_{0f}{}^c = 2\langle t_{2g}(xy)|x|t_{1u}(y)\rangle$. The oscillator strength is computed from the standard relation

$$f = \tfrac{2}{3}\Delta E\mu^2$$

where all quantities are in atomic units and

$$\mu^2 = (\mu_{0f}{}^x)^2 + (\mu_{0f}{}^y)^2 + (\mu_{0f}{}^z)^2$$

Since the SCF wave function for the ground state was obtained without the diffuse functions added for the IVO calculations, it is possible that the transition moments for excitations to Rydberg orbitals could be underestimated.

Results and Discussion

The Positive Ions of SF_6. The highest occupied orbital of SF_6 in the Hartree-Fock calculations (Tables I and II) is the $1t_{1g}$ orbital. The ionization potentials obtained from the orbital energies according to Koopmans' theorem increase in the order $1t_{1g} < 5t_{1u} < 3e_g, 1t_{2u} < 1t_{2g} < 4t_{1u}$. This order may be compared with the other ab initio Hartree-Fock calculations[10,11] on SF_6 (Table I). All calculations included 3d functions on the sulfur, but the calculations by Roos and by von Niessen et al. used a more extensive basis as reflected in the total energies (Table I). These may be compared to the lower total energy of −994.0287 obtained in the present basis. Slightly different geometries were used in all these calculations. The ordering of orbital energies in the present calculation is very similar to the previous results of Roos and von Niessen.

Self-consistent calculations on the ions were performed at the SF_6 geometry to determine the effect of using "frozen" ground state orbitals in the Koopmans' theorem approximation. The SCF results (Table II) maintain the original order

Table III. Orbital Energies (in eV) of the Virtual Orbitals of SF_6 from IVO Calculations[a]

Excitation orbital (ϵ_k)	$6a_{1g}$ (σ*)	$7a_{1g}$ (4s)	$8a_{1g}$ (5s)	$6t_{1u}$ (4p)	$7t_{1u}$ (5p)	4_{eg} (3d)	$2t_{2g}$ (3d)
		Singlet States					
$1t_{1g}$ (−19.15) →	−5.76	−2.51	−1.21	−2.10	−0.94	−1.26	−1.34
$5t_{1u}$ (−19.97) →	−5.13	−2.45	−1.19	−2.10	−0.94	−1.27	−1.34
$3e_g$ (−20.39) →	−4.23	−2.26	−1.16	−2.13	−0.97	−1.26	−1.34
$1t_{2u}$ (−20.39) →	−5.72	−2.50	−1.20	−2.10	−0.95	−1.26	−1.34
$1t_{2g}$ (−23.30) →	−5.84	−2.50	−1.20	−2.11	−0.96	−1.26	−1.34
$4t_{1u}$ (−25.64) →	−5.29	−2.40	−1.18	−2.12	−0.97	−1.26	−1.35
		Triplet States					
$5t_{1g}$ (−19.15) →	−6.10	−2.53	−1.21	−2.16	−1.02	−1.27	−1.35
$5t_{1u}$ (−19.97) →	−6.18	−2.53	−1.21	−2.16	−1.03	−1.27	−1.35

[a] The occupied orbitals and their orbital energies from the Hartree-Fock calculation are listed in the first column.

but generally predict ionization potentials about 0.5 eV smaller than the orbital energies.

GVB-CI calculations for the positive ions were carried out using the GVB(6) orbitals of SF_6 as discussed in the section on computational details. The GVB-CI results in Table II give the same ordering of states as predicted from orbital energies, with the exception of the ^2E_g state, which now appears at higher energy than the $^2T_{2u}$ state, the reverse of the preceding results. With the exception of this ^2E_g state the GVB-CI calculations included about 2 eV more correlation energy in the ions than in the neutral molecule so that the resulting IP's differed by only 1 to 1.5 eV from the experimental values.

For other systems (e.g., N_2^+ and O_3^+) where application of Koopmans' Theorem gives the incorrect ordering of the ion states, GVB-CI calculations have produced the correct ordering.[17,18] In these cases, the ions were formed by removing an electron from either a π-bonding orbital or a lone-pair orbital (e.g., the $1\pi_u$ and $3\sigma_g$ orbitals in N_2^+). Since there is more correlation energy associated with the π electrons than with the lone-pair electrons, Koopmans' theorem may give the wrong order if the levels are close.

In the case of SF_6, however, all the orbitals are essentially lone pair fluorine orbitals, the t_{1g}, t_{2u}, and t_{2g} arising from 2p π orbitals, the $3e_g$ from 2p σ orbitals, and the $5t_{1u}$ from 2p π orbitals with some 2p σ admixture. Since the GVB-CI includes predominantly σ orbital correlations, it is perhaps not surprising that the ^2E_g state, with one less σ electron, is placed at higher energy.

These results, which are based on variational wave functions for each state, are in agreement with the results of von Niessen et al.[11] who used many-body perturbation theory (MBPT) to determine the contributions to the IP directly. The IP's from the GVB-CI calculation are generally 0.5 eV larger in magnitude than the MBPT results, although the same ordering of the states is obtained. Since the two basis sets are comparable, the differences can be attributed to the use of more virtual orbitals in the MBPT than the six virtual orbitals used here and to differences in the perturbative and variational approaches.

In the experimental photoelectron spectrum[5,6] there are four main peaks in the 15-20-eV region: one at 15.7 eV, an intense peak at 17.0 eV, a double-humped feature at 18.6 eV, and another at 19.8 eV. The theoretical calculations place *five* states of SF_6^+ in this vicinity (when one allows for the fact that the orbital energies predict IP's which are several electron volts too large). Two alternative assignments have been advanced for the spectra. Potts et al.[5] attribute the double-humped feature to two separate states and assign the intense 17.0-eV peak to a single state. Gelius[6] suggests that the double peak is due to vibronic interactions and that the intense peak is the sum of two states. This presumes that relatively equal intensities might be expected for orbitals which are primarily fluorine 2p in character.

Table IV. Calculated Term Values for Excited State Orbitals of SF_6

Orbital	Rydberg designation	Range of term values, cm^{-1}
$6a_{1g}$	σ*	34 100-47 100
$7a_{1g}$	4s	18 200-20 200
$8a_{1g}$	5s	9 300-9 700
$6t_{1u}$	4p	16 900-17 200
$7t_{1u}$	5p	7 600-7 800
$4e_g$	3d	10 200-10 200
$2t_{2g}$	3d	10 900-10 900

The present results and the MBPT results would be more consistent with the latter interpretation and would lead to the assignment of the 15.7 eV peak to the $1t_{1g}$ orbital and the intense peak at 17.0 eV to the $5t_{1u}$ and $1t_{2u}$ orbitals. The $3e_g$ and $1t_{2g}$ levels would then account for the next two peaks, respectively. Definitive assignments of the photoelectron spectrum will ultimately depend on reliable theoretical estimates for the intensities as well as positions of the observed peaks.

Excited States of SF_6. The energies of the excited state orbitals (ϵ_l's) of SF_6 are presented in Table III. Although they vary depending upon which orbital was removed to form the SF_6^+ core, the same sequence is observed in all cases

$$6a_{1g} < 7a_{1g} < 6t_{1u} < 2t_{2g}, 4e_g < 8a_{1g} < 5t_{1u}$$

The quantities $-\epsilon_l$ correspond to the spectroscopic term values of the excited state orbitals (Table IV). As shown in the table, the lowest $6a_{1g}$ orbital varies by as much as 13 000 cm^{-1} depending on which ground state orbital is excited. The term values for the higher orbitals are less and less sensitive to the nature of the ion core as the ionization continuum is approached.

A qualitative notion of the excited state orbitals can be obtained by considering their spatial extent as shown by the second moments in Table V. The $6a_{1g}$ orbital has a second moment ($3.28a_0^2$) characteristic of the occupied valence orbitals of the system. Since an examination of the expansion coefficients shows it to have considerable S-F antibonding character, the $6a_{1g}$ orbital will also be designated σ*. All the higher orbitals have spatial extents ($>20a_0^2$) characteristic of diffuse Rydberg orbitals (4s, 4p, etc.). In this notation the

Table V. Spatial Extent of the Excited State Orbitals of SF_6 as Shown by the Calculated Second Moments[a]

Orbital	Rydberg designation	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
$6a_{1g}$		3.28	3.28	3.28
$7a_{1g}$	4s	26.74	26.74	26.74
$8a_{1g}$	5s	130.5	130.5	130.5
$6t_{1u}(x)$	4p	56.99	19.07	19.07
$4e_g(x^2-y^2)$	3d	47.50	47.50	15.87
$2t_{2g}(xy)$	3d	47.15	47.15	15.73

[a] All units are in bohr^2.

Table VI. Comparison of the Ionization Potentials of SF_6 from the Calculated Orbital Energies with Two Possible Assignments of the Photoelectron Spectra[a]

				Alternate assignment	
Orbital	$-\epsilon_i$	Exptl	$\Delta\epsilon_1$[b]	Exptl	$\Delta\epsilon_2$[b]
$1t_{1g}$	19.2	15.7	3.5	15.7	3.5
$5t_{1u}$	20.0	17.0	3.0	17.0	3.0
$1t_{2u}$	20.4	17.0	3.4	18.6	1.8
$3e_g$	20.4	18.6	1.8	18.4	2.0
$1t_{2g}$	23.3	19.8	3.5	19.8	3.5
$4t_{1u}$	25.6	22.9	2.7	22.9	2.7

[a] All values are in eV. [b] $\Delta\epsilon$ = IP(calcd) − IP(exptl).

above sequence becomes

$$\sigma^* < 4s < 4p < 3d < 5s < 5p$$

The Rydberg orbitals (4s, 4p, etc.) are labeled here by drawing the analogy with the states of the sulfur atom as opposed to fitting the calculated term values to a Rydberg series.

The presence of low-lying σ^* valence orbitals in other halogen compounds has been suggested in several experimental assignments,[19-24] but the existence of such a level in SF_6 was unexpected. The work of Nostrand and Duncan[2] and of Robin[14] presumed the lowest states of the molecule to be the first member of a Rydberg series. The existence of a stable σ^* level in a saturated molecule such as SF_6 must owe its existence to the highly polar S^+F^- bonds of the system. The electropositive S center would then stabilize the σ^* orbital, which has more amplitude on the sulfur, since the σ bonding orbital has more fluorine character. One might anticipate that excitations into the σ^* orbital would result in dissociative excited states.

Electronic transitions attributed to n → σ^* or $\sigma \rightarrow \sigma^*$ excitations have been observed in alkyl halides (X = Cl, Br, I) at energies below the normal Rydberg states.[19-24] The insensitivity of these transitions to the surrounding medium[22] has been taken as evidence of their valence-state nature. Apparently no such σ^* levels have been assigned in the alkyl fluorides, however, and there has been little theoretical work to confirm these assignments on the basis of rigorous calculations.

The calculated excitation energies are just the difference between the occupied and virtual levels given in Table III. To compare with the experimental spectrum it is customary to correct the occupied levels (ϵ_k) by the difference in the calculated and experimental IP's. Based on the assignment of the experimental IP's from the analysis in the previous section, energy shifts ($\Delta\epsilon_1$ in Table VI) have been determined to adjust the computed transition energies. (The alternative assignment of the t_{2g} and e_g levels to the 18.6-eV peak in the photoelectron spectrum would yield the energy shifts $\Delta\epsilon_2$ in the table.) When these shifts are included one obtains the transition energies given in Table VII, where the dipole-allowed transitions are underlined.

The following analysis of the spectrum of SF_6 assumes the observed peaks are due to dipole-allowed transitions, but the possibility exists that some of the peaks are vibronically induced. The computed matrix elements used to compute the oscillator strengths are listed in Table VIII along with the degeneracy factor to give the overall matrix element between initial and final states. The transition-dipole matrix elements are expected to fall off in magnitude for the higher members of a Rydberg series, since the oscillator strength should have a $1/n^3$ dependence on principal quantum number. The limitations of the basis set become evident for the highest virtual orbitals of a particular symmetry, where the transition moments actually start to increase. For this reason only rough estimates are possible for the 5s, 5p, and higher levels. The orbital energies, on the other hand, are much less sensitive to the orbital exponents of the basis and thus are likely to be more reliable.

The lowest excited states of SF_6 (Table IX) are the $^3T_{1g}$ (9.6 eV) and $^1T_{1g}$ (9.9 eV) states arising from the $1t_{1g} \rightarrow 6a_{1g}$ (σ^*) excitation. At slightly higher energies are the $^3T_{1u}$ (10.8 eV) and $^1T_{1u}$ (11.8 eV) states from the $5t_{1u} \rightarrow \sigma^*$ excitation. The dipole allowed $^1T_{1u}$ state is undoubtedly responsible for the first major peak at 11.73 eV (see Table IX) in the UV spectrum and the 11.54-eV peak in the electron impact energy loss spectrum. Chutjian et al.[25] observe features at 9.8 and 12.9 eV in the electron loss spectra at large scattering angles and low incident energies characteristic of forbidden states. The former peak could arise from the symmetry-forbidden $^1T_{1g}$ state (9.9 eV)

Table VII. Calculated Excitation Energies for SF_6[a]

	$6a_{1g}$ (σ^*)	$7a_{1g}$ (4s)	$8a_{1g}$ (5s)	$6t_{1u}$ (4p)	$7t_{1u}$ (5p)	$4e_g$ (3d)	$2t_{2g}$ (3d)
			Singlet States				
$1t_{1g} \rightarrow$	9.9	13.1	14.4	$\underline{13.6}$	$\underline{14.7}$	14.4	14.3
$5t_{1u} \rightarrow$	$\underline{11.8}$	$\underline{14.5}$	$\underline{15.8}$	14.9	16.0	$\underline{15.7}$	$\underline{15.6}$
$3e_g \rightarrow$[b]	14.4	16.3	17.4	$\underline{16.5}$	$\underline{17.6}$	17.3	17.2
$1t_{2u} \rightarrow$[b]	11.3	14.5	15.8	14.9	16.0	$\underline{15.7}$	$\underline{15.6}$
$1t_{2g} \rightarrow$	14.0	17.3	18.6	$\underline{17.7}$	$\underline{18.8}$	18.5	18.4
$4t_{1u} \rightarrow$	$\underline{17.6}$	$\underline{20.5}$	$\underline{21.8}$	20.8	22.0	$\underline{21.7}$	$\underline{21.6}$
			Triplet States				
$1t_{1g}$	9.6	13.1	14.4	13.6	14.7	14.4	14.3
$5t_{1u}$	10.8	14.5	15.8	14.9	16.0	15.7	15.6

[a] All quantities have been corrected by the appropriate amounts to give the experimental ionization potentials ($\Delta\epsilon_1$ in Table VI). Dipole-allowed transitions are underlined. [b] If the alternative assignment for the photoelectron spectrum is assumed, the excitation energies from the $1t_{2u}$ and $3e_g$ orbitals should be increased by 1.6 and −0.2 eV, respectively.

Table VIII. Dipole Transition Matrix Elements between the Occupied and Virtual Orbitals of SF_6

Occupied orbital	Virtual orbital	μ component	μ_{ij}, au[a]	Space-spin factor
$1t_{1g}(xz)$	$6t_{1u}(z)$	x	0.1522	2
$5t_{1u}(z)$	$6a_{1g}$	z	0.6069	$2^{1/2}$
	$7a_{1g}$	z	0.0937	$2^{1/2}$
	$4e_g(z^2)$	z	0.0669	$2^{1/2}$
	$2t_{2g}(xz)$	x	0.0678	$2^{1/2}$
$1t_{2u}(z)$	$4e_g(z^2)$	z	0.0669	$2^{1/2}$
	$2t_{2g}(xz)$	x	0.0135	2
$3e_g(z^2)$	$6t_{1u}(z)$	z	0.2272	$2^{1/2}$
$1t_{2g}(xz)$	$6t_{1u}(z)$	x	0.0542	2
$4t_{1u}$	$6a_{1g}$	z	0.5945	$2^{1/2}$
	$7a_{1g}$	z	0.2018	$2^{1/2}$

[a] 1 au = 2.541 58 D.

mentioned above. The $^1T_{1g}$ state from the $1t_{1g} \rightarrow 7a_{1g}$ (4s) excitation at 13.1 eV would then correspond to the 12.9 eV feature.

Three weak features in the UV spectrum at 13.3, 14.3, and 15.2 eV and in the electron energy loss spectrum[4] at 13.3, 14.3, and 14.9 eV are in the same vicinity as the calculated $1t_{1g} \rightarrow 6t_{1u}$ (13.6 eV), $5t_{1u} \rightarrow 7a_{1g}$ (14.5 eV), and $1t_{1g} \rightarrow 7t_{1u}$ (14.7 eV) transitions, all of which are dipole allowed with oscillator strengths between 0.02 and 0.09 (see Table IX).

The bands at 15.7 and 16.9 eV are assigned to the $3e_g \rightarrow 6t_{1u}$ and $4t_{1u} \rightarrow 6a_{1g}$ (σ^*) transitions at 16.5 eV (f = 0.12) and 17.6 eV (f = 0.92), respectively. The strong band observed at 23 eV is most likely the $5a_{1g} \rightarrow 6t_{1u}$ transition. The present calculations do not extend into this energy region, but an estimate of 24.9 eV for this band is obtained from the $5a_{1g}$ IP (27.0 eV) and the $6t_{1u}$ (4p) term value (2.1 eV). The weak feature at 20 eV may correspond to the $4t_{1u} \rightarrow 7a_{1g}$ Rydberg excitation calculated at 20.5 eV.

The present assignments differ from Robin's analysis,[14] which assumed the first four-electron energy-loss peaks between 11.5 and 15.2 eV corresponded to excitations from the four highest occupied orbitals into the lowest s Rydberg orbital with a term value of 30 000 cm^{-1}. Since only one of these transitions ($t_{1u} \rightarrow a_{1g}$) is allowed, the other would necessarily need to acquire intensity by vibronic mixing. Alternatively the possibility exists that the optical selection rules are not as stringent in the electron scattering process. The analysis of Simpson et al.,[4] where forward scattering of 400-eV electrons was observed, should yield reliable optical absorption data and in fact they observe the same peaks found in the UV spectrum.

The present results for excitation into the lowest a_{1g} orbital, 9.9, 11.3, 11.8, 14.0, and 14.4 eV from the highest t_{1g}, t_{2u}, t_{1u}, t_{2g}, and e_g orbitals, respectively (Table VII), do not appear to be in as close accord with the observed spectral peaks as the assignments in Table IX. The assumption of a constant term value of ~30 000 cm^{-1} for the $6a_{1g}$ level led Robin to assign the strong peak at 11.5 eV as an excitation from the highest occupied orbital. Since the highest occupied orbital is the t_{1g}, however, it is unlikely that the forbidden $t_{1g} \rightarrow a_{1g}$ transition (calculated at 9.9 eV) is responsible for this strong peak. In this regard it is interesting that the calculated term values for the $6a_{1g}$ orbital are largest (see Table III) for excitations from orbitals which have no σ(S-F) character, t_{1g} (46 400 cm^{-1}) and t_{2u} (46 100 cm^{-1}); smallest for the e_g orbital which has *only* σ(S-F) character (34 100 cm^{-1}); and intermediate (41 300 cm^{-1}) for the $5t_{1u}$ orbital which contains *partial* σ(S-F) character. Although the spectra of many fluorinated compounds have been interpreted in terms of excitations to an s orbital with a term value of ~30 000 cm^{-1}, complications can arise when low-lying σ^* virtual orbitals lie in the same region

Table IX. Comparison of the UV and Electron-Impact Spectra of SF_6 with the Calculated Results[a]

	Calcd results		UV spectra[b]		Electron-impact spectra[c,d]	
Orbital excitation	ΔE, eV	Oscillator strength (f)	ΔE, eV	Rel intensity	ΔE, eV	Rel intensity
		Lowest Dipole-Forbidden States				
$^3[1t_{1g} \rightarrow 6a_{1g}\ (\sigma^*)]$	9.6					
$1t_{1g} \rightarrow 6a_{1g}\ (\sigma^*)$	9.9				~9.8	
$^3[5t_{1u} \rightarrow 6a_{1g}\ (\sigma^*)]$	10.8					
$1t_{2u} \rightarrow 6a_{1g}\ (\sigma^*)$	11.3					
$1t_{1g} \rightarrow 7a_{1g}$ (4s)	13.1				~12.9	
		Dipole-Allowed States				
$5t_{1u} \rightarrow 6a_{1g}\ (\sigma^*)$	11.8	0.64	11.73	m (f = 0.29)	11.54	s
$1t_{1g} \rightarrow 6t_{1u}$ (4p)	13.6	0.09	13.27	w (f = 0.05)	13.30	m
$5t_{1u} \rightarrow 7a_{1g}$ (4s)	14.5	0.02	14.28	w (f = 0.13)	14.35	m
$1t_{1g} \rightarrow 7t_{1u}$ (5p)	14.7	~0.05	15.16	w (f = 0.10)	14.90	w
$5t_{1u} \rightarrow 2t_{2g}$(3d)	15.6	0.04				
$1t_{2u} \rightarrow 2t_{2g}$(3d)	15.6	10^{-3}				
$5t_{1u} \rightarrow 4e_g$(3d)	15.7	0.01				
$1t_{2u} \rightarrow 4e_g$(3d)	15.7	0.01				
$5t_{1u} \rightarrow 8a_{1g}$(5s)	15.8	~0.01				
$3e_g \rightarrow 6t_{1u}$(4p)	16.5	0.12	~15.7	m	16.0	s
$3e_g \rightarrow 7t_{1u}$(5p)	17.6	~0.06				
$4t_{1u} \rightarrow 6a_{1g}(\sigma^*)$	17.6	0.92	~16.9	s	17.4	s
$1t_{2g} \rightarrow 6t_{1u}$(4p)	17.7	0.01				
$1t_{2g} \rightarrow 7t_{1u}$(5p)	18.8	~0.01				
$4t_{1u} \rightarrow 7a_{1g}$(5s)	20.5	0.12	~20	w		
$5a_{1g} \rightarrow 6t_{1u}$(4p)	(~25)		23.1	s	~23	s

[a] $^3[\ ]$ denotes triplet states. Calculated results have been corrected as in Tables VI and VII. [b] References 2-4. In ref 4, the optical spectrum was derived from the electron impact data. [c] References 4 and 14. [d] Reference 25.

Table X. Orbital Energies of Occupied (ϵ_k) and Virtual (ϵ_l) Orbitals for Core Excitations in SF_6 (in eV)[a]

		ϵ_l's						
Excitation	ϵ_k	$6a_{1g}$	$7a_{1g}$	$8a_{1g}$	$6t_{1u}$	$7t_{1u}$	$4e_g$	$2t_{2g}$
$1s_S \rightarrow$	−2516	−13.3	−2.7	−1.3	−10.4	−2.1	−1.3	−1.4
$1s_F \rightarrow$[c]	−718.3 (−695)	−7.3 (−7)	−2.6	−1.2	−2.2 (−1)	−1.3	−1.3	−1.4
$2s_S \rightarrow$	−256.6 (−244.7)	−11.0	−2.7	−1.2	−8.1	−2.1	−1.3	−1.4
$2p_S \rightarrow$	−193.4 (−181.8)	−12.1 (−9.6)	−2.7	−1.2	−7.7	−2.1	−1.3	−1.4

[a] Experimental binding energies relative to the ionization threshold are given in parentheses. [b] See ref 26. [c] Nearly identical results were obtained by exciting either the $2a_{1g}$ or $1t_{1u}$ fluorine 1s orbitals.

as Rydberg orbitals. Clearly a full understanding of all these intricacies will await more detailed theoretical and experimental studies.

The spatial extent of the excited state orbitals (Table V) indicates that only the $6a_{1g}$ (σ^*) orbital would be well-described by the basis in Gianturco's calculation. Indeed his excitation energies for the transitions $5t_{1u} \rightarrow 6a_{1g}$ (11 eV) and $4t_{1u} \rightarrow 6a_{1g}$ (17 eV) are in reasonable agreement with the present results. In contrast excitation energies to higher orbitals are at least 4-5 eV higher than the uncorrected values reported here and 8-10 eV higher than the energies with corrections for the IP's. For example, the $t_{1g} \rightarrow 6t_{1u}$ excitation is placed at 21 eV compared to 17.1 (uncorrected) and 13.6 (corrected). Curiously a large transition moment was reported in the earlier calculation for the dipole-forbidden $t_{2u} \rightarrow a_{1g}$ transition.

The distinction between valence and Rydberg excited states noted here in the UV spectrum of SF_6 has an analogy in the x-ray absorption spectrum according to an interpretation by Dehmer[26] and Nefedov.[27] In this analysis one distinguishes between excitations from core orbitals to diffuse "outer well" states and excitations from core orbitals to "inner well" states localized within an effective barrier of the electronegative fluorine atoms. Very little intensity would be expected from excitations to the "outer well" state having small overlap with the core, whereas appreciable intensity could arise from the "inner well" states near the core region.

To determine the validity of the valence-Rydberg ("inner well-outer well") analogy in x-ray absorption spectra, IVO calculations were performed by removing an electron from a sulfur 1s, 2s, or 2p or fluorine 1s orbital. The binding energies (in eV) of the virtual orbitals in the field of these respective ion cores are shown in Table X. Again we observe an extremely stable (−7 to −13 eV) bound $6a_{1g}$ level similar to the $6a_{1g}$ (σ^*) level discussed earlier in the analysis of the UV spectrum. In fact the binding energies are greater than the values of −4 to −6 eV (34 000-47 000 cm^{-1}) calculated when the ion core was formed by removing a fluorine nonbonding electron.

In addition a very stable $6t_{1u}$ level (−8 to −10 eV) also appears when the core "hole" state is localized on the sulfur. When a 1s fluorine "hole" is formed, however, the $6a_{1g}$ and $6t_{1u}$ levels are destabilized at least 4 and 6 eV, respectively, relative to an excitation from a sulfur orbital. Since these $6a_{1g}$ and $6t_{1u}$ orbitals are located primarily within the SF_6 octahedron, it is perhaps not surprising that the states are bound most strongly when the "hole" is formed on the central sulfur atom. The remaining virtual orbitals (Table X) have binding energies comparable to the values found (Table IV) for valence excitations.

The calculated results in Table X are in reasonable agreement with some features observed in the x-ray absorption spectrum.[9b,26] In the F 1s and S 2p spectra peaks at 7 and 10 eV below the respective ionization thresholds are observed (calculated binding energies are 7 and 12 eV) which correspond to excitations into the $6a_{1g}$ orbital. Dehmer attributes $2a_{1g}$ ($1s_F$) $\rightarrow 6t_{1u}$ and $2t_{1u}$ ($2p_s$) $\rightarrow 6t_{1u}$ transitions to peaks 1 and 3 eV, respectively, below threshold, although the present results would place the $2t_{1u} \rightarrow 6t_{1u}$ transition somewhat lower in energy.

The absorption spectra of gaseous and solid SF_6 by Blechschmidt et al. show little effect on the core-to-valence transitions in the x-ray region as one would expect. The fact that the transitions in the 10-20-eV region are significantly perturbed in the solid can be taken as evidence that (a) the occupied valence orbitals themselves are affected and/or (b) the excited state orbitals are diffuse. Blechschmidt et al. cite the former reason, but in addition it can be noted that several of the calculated Rydberg states lie in this region. A strong peak in the solid reflection spectrum near 17 eV is consistent with the calculated valence $4t_{1u} \rightarrow \sigma^*$ transition at 17.6 eV, and the data did not extend to low enough energy to probe the $5t_{1u} \rightarrow \sigma^*$ transition at 11.5 eV.

Summary

The orbital energies of SF_6 and SCF calculations on SF_6^+ predict the states of the ion increase in the order $1t_{1g} < 5t_{1u} < 1t_{2u}, 3e_g < 1t_{2g} < 4t_{1u}$. The inclusion of electron correlation effects leads to the sequence $1t_{1g} < 5t_{1u}, 1t_{2u} < 3e_g < 1t_{2g} < 4t_{1u}$ from GVB-CI calculations, which are also in agreement with a recent many-body treatment.

The lowest excited state orbitals are in increasing order $6a_{1g}$ (σ^*), $7a_{1g}$ (4s), $6t_{1u}$ (4p), $2t_{2g}$ (3d), $4e_g$ (3d), $8a_{1g}$ (5s), and $7t_{1u}$ (5p). All but the lowest orbital are diffuse Rydberg orbitals, while the $6a_{1g}$ corresponds to a valence antibonding orbital. The lowest excited state of SF_6 is the dipole-forbidden $^1T_{1g}$ state arising from the $1t_{1g} \rightarrow 6a_{1g}$ excitation, while the lowest dipole-allowed $^1T_{1u}$ state corresponds to the $5t_{1u} \rightarrow 6a_{1g}$ excitation.

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A Molecular Orbital Study of Monomeric Metaphosphate. Density Surfaces of Frontier Orbitals as a Tool in Assessing Reactivity

Leslie M. Loew* and William R. MacArthur

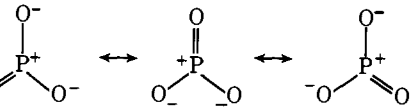
Contribution from the Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901. *Received May 3, 1976*

Abstract: The geometry, bonding, charge distribution and reactivity of monomeric metaphosphate, a unique anionic Lewis acid, are explored with ab initio and semiempirical MO calculations. Comparison with calculations on the isostructural and congeneric nitrate anion places many of these features in perspective. Among the key findings are: (1) a large contribution from 2p-3d π bonding affects not only the P-O overlap population but also the bond length; (2) 2p-3p π bonding is significantly (but not drastically) diminished in PO_3^- relative to 2p-2p π bonding in NO_3^-; (3) the electrophilic reactivity of this unstable intermediate may be ascribed to the presence of a low lying unoccupied acceptor orbital of σ symmetry which is nearly degenerate with the usual π^* MO. Isodensity surface plots and plots of density in a plane are presented for the acceptor orbitals of PO_3^- and NO_3^-; these allow a thorough qualitative perturbation theory analysis of their relative reactivities. Extensions of this analysis to other systems are suggested.

The monomeric metaphosphate anion is believed to be a key intermediate in many of the phosphoryl transfer reactions occurring in biological systems.[1] Both kinetic[2] and trapping[3] experiments have amply demonstrated a finite lifetime for this and closely related species; recently in fact, the preparation[4] and x-ray structure determination[5] of some highly substituted neutral analogues were reported.

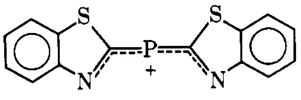
The use of theory to examine unstable species can provide accurate predictions of potential experimental results. In this work we probe the properties of this experimentally elusive anion via several molecular orbital techniques including an ab initio SCF-MO method using a Gaussian orbital basis set. Most importantly, examination of the low energy unoccupied MO's suggests some interesting aspects of the reactivity of PO_3^- and its analogues, including the surprisingly strong electron acceptor properties of their σ systems. This is achieved with the aid of computer-generated three-dimensional probability density plots and exemplifies an approach of potentially broad applicability. While the major thrust of our work is based on qualitative examinations of the calculations, the derived geometry and charge distribution, although approximate, will allow better informed speculations on the conditions under which the intermediate is stabilized.

In addition to these properties, the calculations reveal the nature of the bonding in this unique anionic Lewis acid. Specifically, its electronic structure is examined for the importance of 2p-3p π bonding as illustrated by resonance structures **1**.



1a **1b** **1c**

The origin of the apparent ineffectiveness of π bonds between second and third period elements has long been the subject of theoretical[6] and experimental[7] interest. A recent surge of activity in this field has included the preparation of phosphamethine cyanines,[8] **2**, phosphabenzene,[9] **3**, bis(dimethylamido)phosphinium cation, **4**,[10] a metaphosphordiimidic amide, **5**,[11] and the detection of a silaethylene, **6**, by low temperature infrared spectroscopy.[12] Semiempirical and ab initio MO calculations of systems **3**[13,14] and **6**[15,16] have also appeared and aid considerably in the correlation of spectroscopic data and relative reactivities. In this work the general problem of 2p-3p π bonding is probed by direct comparison of the bonding in PO_3^- with the results of similar calculations on the congeneric NO_3^-.



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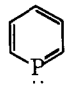

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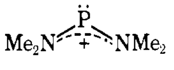
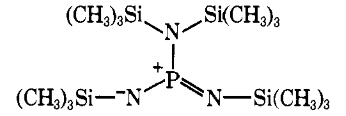


$Me_2N\overset{..}{\overset{P}{\cdots}}\overset{+}{}NMe_2$

4



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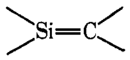

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The system also provides a new environment for assessing the importance of d-orbital participation. This, too, has been the subject of much recent effort and controversy with cases being made for[17] and against[18] depending on the system studied or the criterion chosen for judgement. It might be expected that for our system the electron deficiency of the central phosphorus could cause a contraction of d orbitals leading to substantial π interaction with unshared electron pairs on the oxygens (structures **7**). Examination of d-orbital effects in nitrate ion provides a good frame of reference as well as an