hedrally coordinated Fe(III) exists in ferritin. While perhaps fortuitous it can also be pointed out that of the three possible oxo, hydroxo-bridged models the absorption spectrum of the Fe–alanine compound most closely resembles that of the "Spiro–Saltman Ball."

In Table II we have tabulated the magnetic results and Mössbauer parameters for the three model systems, the "Spiro–Saltman Ball" and ferritin. Without question both the μ/Fe^{3+} and the $-J$ for the Fe(III)–alanine complex most closely resemble the values found for the latter two members of Table II. In addition the similarity of these species is reinforced by the Mössbauer data. This suggests that the $[Fe_3O]^{7+}$ unit must be considered as a strong candidate for the basic "monomeric" unit in both the "Spiro–Saltman Ball" and ferritin.

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Received October 12, 1973

Use of the CNDO Method in Spectroscopy.
XI. Photoelectron Spectra

Sir:

The most widely applied theoretical method in the assignment of bands in photoelectron (PE) spectra and in their interpretation[1] is based on the use of Koopmans' theorem.[2] Although many authors have long been aware of the shortcomings of this procedure,[3] the lack of reasonably reliable and readily applied methods for the calculation of the doublet states of the molecular ions has retarded progress in the interpretation of PE spectra and forced many authors into the use of Koopmans' theorem in spite of its undesirability.

We have now developed two semiempirical methods for calculation of the energies (and wave functions) of doublet states, which are readily applicable to the calculation of the molecular ions of molecules of first-row elements with closed shell ground states. Both methods are based on the CNDO/S method;[4] the first[5] is quite analogous to the closed shell CNDO/S method, using a SCF calculation of the ionic ground state by the Roothaan open shell restricted Hartree–Fock formalism,[6] followed by a limited CI calculation using singly excited configurations. The second method[7] involves the direct

(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., Chapter 1 and Chapter 4.

(2) T. A. Koopmans, *Physica*, **1**, 104 (1933).

(3) *Cf.* ref 1, pp. 6–7; *cf.* also M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *Tetrahedron Lett.*, **47**, 4659 (1973).

(4) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968); R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972).

(5) H. M. Chang and H. H. Jaffé, *Chem. Phys. Lett.*, **23**, 146 (1973).

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(7) H. H. Jaffé, H. M. Chang, and C. A. Masmanidis, *J. Comput. Phys.*, in press.

SCF calculation of excited doublet states, again by the Roothaan method.[6] In this communication we report the first application of these methods to PE spectra.

The PE spectral information is usually reported as the ionization potential from the molecular ground state to the ion state J; this quantity can be decomposed into two terms

$$I_J = I_0 + X_J \qquad (1)$$

where I_0 is the ionization potential to the ion ground state and X_J the energy of the ion state J above its ground state. Ionization potentials are most commonly obtained by using Koopmans' theorem; the CNDO/S method appears to be the best of the common semiempirical methods (without special parametrization) for obtaining ionization potentials,[8] but the values obtained are usually significantly too high. The SCF procedure for the ion ground state gives another independent estimate of the vertical ionization potential as the difference of the total energy of the ground states of the neutral molecule and the ion. The ionization potentials so obtained are generally somewhat below the Koopmans' theorem values but are still uniformly high. These results are summarized in Table I.

Table I. Calculated First Ionization Potentials by SCF Procedure and Koopmans' Theorem

| | Ionization potential | | |
Molecule	SCF	Koopmans' theorem	Exptl
Benzene	10.4	10.8	9.24[a]
s-Trifluorotriazine	11.3	11.5	10.3[b]
s-Triazine	12.1	12.5	10.41[b]
s-Trifluorotriazine	13.2	13.5	12.0[b]
Pyridine	10.5	10.8	9.31[a]
Pyrimidine	11.1	11.4	9.32[c]	10.2[a]
Pyrazine	10.6	10.9	9.22[c]	9.36[a]
Pyridazine	11.0	11.0	8.71[c]	8.90[a]

[a] Reference 12. [b] Reference 15. [c] Reference 14.

In what follows we shall ignore the first term of eq 1 and restrict ourselves to a consideration of the second term, X_J, i.e., the *relative* positions of the bands in the PE spectrum or the spacing of the doublet states of the ion. The expression for the PE cross section is given as[9]

$$\sigma_{J0} = \frac{8\pi^3 e^3 \nu}{3c} |\langle {}^1\Psi_0 | \sum_i \mathbf{r}_i | {}^1\Psi_J \rangle|^2$$

where e, ν, and c are the electronic charge, the frequency of the ionizing radiation, and the velocity of light, respectively.

In the present work we take ${}^1\Psi_0$ as a single Slater determinant of order n. ${}^1\Psi_J$ is a proper singlet eigenfunction of an excited state of the n electron system in which $n - 1$ electrons occupy molecular orbitals in the usual sense of the word and the remaining one-electron wave function is a proper wave function for a free electron.[10] If the molecular orbitals making up ${}^1\Psi_0$ and ${}^1\Psi_J$ are orthogonal, one is led to the conclusion that

(8) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **50**, 563 (1969).

(9) L. L. Lohr and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 7241 (1970).

(10) (a) D. R. Bates, U. Öpic, and G. Poats, *Proc. Phys. Soc., London, Sect. A*, **66**, 1113 (1953); (b) A. Dalgarno, *ibid.*, **65**, 663 (1952).

Table II. Relative Doublet State Energies of Photoelectron Active States

Molecule	Koopmans' theorem Symmetry	Energy[a]	Restricted Hartree–Fock Symmetry	Energy[a,b] VO	SCF	Exptl energy[a]
Benzene[c,d]	E$_{1g}$ π	0.0	E$_{1g}$ π	0.0, 0.12	0.0	0.0
	E$_{2g}$ σ	2.60	E$_{2g}$ σ	2.86, 2.96	2.78	2.2
	A$_{2u}$ π	4.72	A$_{2u}$ π	3.68	e	3.1
Hexafluorobenzene[c,d]	E$_{1g}$ π	0.0	E$_{1g}$ π	0.0, 0.22	0.0	0.0
	B$_{2u}$ σ	3.44	A$_{2u}$ π	2.82	e	2.6
	A$_{2u}$ π	3.53	B$_{2u}$ σ	3.53	3.71	3.8
	E$_{2g}$ σ	5.52	E$_{2g}$ σ	4.69, 4.76	4.73	4.5
s-Triazine[c,d]	E' n	0.0	E' n	0.0, 0.97	0.0	0.0
	E'' π	0.37	E'' π	0.57, 1.43	0.51	1.3
s-Trifluorotriazine[c,d]	E'' π	0.0	E'' π	0.0, 1.14	0.0	0.0
	E' n	0.16	E' n	0.11, 1.23	0.13	
Pyridine[f]	A$_2$ π	0.0	A$_2$ π	0.0	0.0	0.0
	B$_1$ π	1.15	A$_1$ n	1.14	0.77	0.12
	A$_1$ n	1.23	B$_1$ π	1.45	1.13	1.14
	B$_2$ σ	3.02	B$_2$ σ	3.31	3.15	2.99
	A$_1$ σ	5.04	B$_1$ π	4.32	e	4.52
	B$_1$ π	6.52				
Pyrimidine[f]	B$_2$ π	0.0	B$_2$ π	0.0	0.0	0.0 0.0
	B$_1$ n$_-$	0.65	B$_1$ n$_-$	0.56	0.61	0.22 0.68
	A$_2$ π	1.22	A$_2$ π	1.18	1.23	0.97 1.50
	A$_1$ n$_+$	1.97	A$_1$ n$_+$	1.85	2.03	1.64 1.66
	A$_1$ σ	4.40	A$_1$ σ	4.12	e	4.20 4.20
	B$_1$ σ	4.53	B$_1$ σ	4.47	e	4.40
	B$_2$ π	5.41	B$_2$ π	4.56	e	
Pyrazine[b,f]	B$_{2g}$ π	0.0	B$_{2g}$ π	0.0	0.0	0.15 0.0
	A$_g$ n$_+$	1.30	A$_g$ n$_+$	0.76	0.66	0.79 0.45
	B$_{1g}$ π	2.52	B$_{1g}$ π	2.23	1.83	1.78 1.72
	B$_{2u}$ n$_-$	3.58	B$_{2u}$ n$_-$	2.91	2.73	3.37 2.14
	B$_{3g}$ σ	4.84	B$_{3u}$ π	3.92	e	3.77 4.3
	B$_{3u}$ π	6.41				
Pyridazine[b,f]	A$_2$ π	0.0	B$_1$ n$_-$	0.0	0.0	0.0 0.0
	B$_1$ n$_-$	0.16	A$_2$ π	0.28	0.11	0.32
	B$_2$ π	0.76	B$_2$ π	1.23	1.20	1.63 1.3
	B$_1$ σ	4.03	A$_1$ n$_+$	1.55	2.20	2.26 2.0
	A$_1$ n$_+$	4.97	B$_2$ π	4.18	e	4.73 4.6
	B$_2$ π	5.24				

[a] All energies in eV. [b] The lower of the VO or SCF values should be taken as the best estimate, since the VO result is not self-consistent, but the SCF result neglects configurational mixing. [c] The two energies given for degenerate states were derived by constraining the wave function to span the irreducible representations of D_{2h} or C_{2v}. [d] See ref 15. [e] Inaccessible to the SCF calculation. [f] See ref 12; for the second experimental value see ref 14.

σ_{J0} vanishes if $^1\Psi_0$ does not contain all the molecular orbitals that $^1\Psi_J$ does. Therefore σ_{J0} vanishes for all but the ground state and the type A excited states of the ion,[11] i.e., those states derived from the doublet ground state by the promotion of an electron from a doubly occupied orbital to the singly occupied one. These are then the only states one expects to appear in the PE spectrum with reasonable intensity.

Recently, several workers have reported ionization potentials for the azines.[12,13] In proposing the assignments of the observed ionization potentials, Dewar and coworkers have relied on a first-order perturbation treatment and Koopmans' theorem.[12] These workers conclude that the first ionization of pyridine and pyrazine involves removal of a π electron and pyridazine and pyrimidine removal of a nonbonding electron. The results are in disagreement with the assignment of Yencha and El-Sayed[13] who considered it to be a π electron which is removed in all four compounds and with that of Heilbronner and coworkers,[14] who considered the first electron ionized to be an n electron in all three diazines.

In Table II, we propose an assignment for the observed PE spectra of pyridine, pyrimidine, pyrazine, and pyridazine in the low energy region. For comparison we have included the Koopmans' theorem results; however, as can readily be seen, these results do not lead to any reasonable interpretation of experiment. The VO and SCF results, however, predict ion states to lie in regions where ionizations are observed by experiment. Our assignment of the ion ground state of these four compounds supports the assignments of El-Sayed.[13] Our VO and SCF calculations are in reasonable agreement with the higher energy states, the predicted energy being generally within 0.2–0.7 eV from the observed value. We feel that, in these compounds, the agreement is sufficient to assign the symmetry of the ion state from the calculated spectra.

The situation is more complicated in the remainder of the compounds listed in Table II. In all these, the highest occupied molecular orbital is doubly degenerate, and consequently the ground state of the ion is doubly degenerate. In this case it is inappropriate to describe the wave function by a single Slater determinant. As a

(11) P. Balk, S. DeBruim, and G. J. Hoijtink, Recl. Trav. Chim. Pays-Bas, 76, 907 (1957); A. Ishitani and S. Nagakura, Theor. Chim. Acta, 4, 236 (1966).
(12) M. J. S. Dewar and S. D. Worley, J. Chem. Phys., 51, 236 (1969).
(13) A. J. Yencha and M. A. El-Sayed, J. Chem. Phys., 48, 3469 (1968).
(14) R. Gleiter, E. Heilbronner, and V. Hornung, Helv. Chim. Acta, 55, 255 (1972).

preliminary attack on this problem, we have constrained the wave functions of the degenerate states to span the C_{2v} or D_{2h} subgroup of the molecular point group rather than the true molecular point group D_{3h} or D_{6h}, so that we can describe the ground state by a single Slater determinant. In the VO procedure this leads to a splitting of the original degeneracy. One could view this splitting as a precursor to the Jahn–Teller splitting which arises when the molecular geometry is distorted in such a way as to lower the symmetry of the molecule to C_{2v} or D_{2h}. In the SCF procedure this problem does not arise; the two components of the degenerate ground state remain degenerate within the estimated precision of the calculations and, since they span different irreducible representations of the subgroup, are not expected to interact, so that the energy may be accepted.

In benzene and its hexafluoro derivative one sees the *pre-Jahn–Teller splitting* of the degenerate states in the VO approximation. The hexafluorobenzene calculations suggest a somewhat different interpretation of the experimental results than that given by Robin, *et al.*,[15] in that the state at 3.8 eV above the ground state is a nondegenerate B_{1u} σ state and the state at 4.5 eV is the doubly degenerate E_{1g} σ state. In triazine, our calculations support the assignment of the ground state as a doubly degenerate n state and the first excited state as a doubly degenerate π state.[15] In trifluorotriazine, our calculations suggest that these two states have become nearly degenerate. Therefore, the first ionization observed represents ionization to both the n and π states. Such an assignment will lead to a fluorine shift of about 2.0 eV, which is in the expected range.[15] It is interesting to note the large pre-Jahn–Teller splitting we are getting in these two compounds compared to benzene and hexafluorobenzene. This same behavior is observed in the experimental spectra.[15]

We are currently extending this work to larger systems and higher energy states. We are also investigating how the optical spectrum of ions can complement PE methods, since states may be observed in the optical spectrum which have vanishing PE cross sections.

(15) M. B. Robin, N. A. Kuebler, and C. R. Brundle in "Electron Spectroscopy," D. A. Sherly Ed., North-Holland Publishing Co., Amsterdam, 1972, pp 351-377.

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Preparation of Macrocyclic Tertiary Amine Complexes of Nickel(II) by Alkylation of Coordinated Amine. Crystal Structure of a Monoazide Bridged Dimer of Ni(N-tetramethylcyclam)²⁺

Sir:

Recently we reported the preparations of **1** and some of its metal complexes.[1] A surprising and disappointing property of these complexes was their lability, which was apparently a result of the set of nitrogen donor configurations that was dictated by the kinetic precesses

(1) E. K. Barefield and F. Wagner, *Inorg. Chem.*, 12, 2435 (1973).

leading to complex formation.[2] Spectroscopic data were consistent with a structure which had all four methyl groups on the same side of the coordination plane defined by the four donor nitrogens.[2] However, we expected that a synthesis that involved N-alkylation of **2** (NiCyclam²⁺) might produce a different set of nitrogen donor configurations and, as a result of this, a more inert complex. This reasoning led us to explore procedures for alkylation of the coordinated amines in this complex and the related systems **3** and **4**.

1
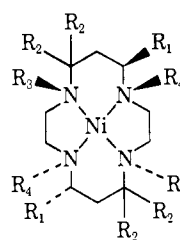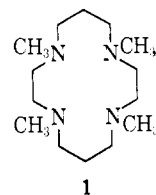
2, R = H
3, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
5, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
6, R = CH_3
8, $R_1 = R_2 = CH_3$; $R_3 = CH_3$; $R_4 = H$
9, $R_1 = R_2 = CH_3$; $R_3 = H$; $R_4 = CH_3$
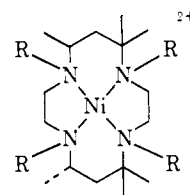
4, R = H
7, R = CH_3

Coordinated amines have no nucleophilic properties; however, removal of a proton generates a nucleophilic amide which may be alkylated.[3] We have found that the base–solvent systems KOH–DMSO[4] and $NaCH_2S(O)CH_3$–DMSO[5] are useful for generating deprotonated forms of **2-4** as well as a variety of other macrocyclic amine complexes of nickel(II) and that these deprotonated forms may be alkylated with several reagents. This communication provides a preliminary account of certain aspects of this work including the results of an X-ray structural determination on a Ni(II) complex of **1** that was prepared by N-alkylation of **2**.

Complexes **2-4** react instantaneously with 1 equiv of $NaCH_2S(O)CH_3$ in DMSO to yield highly colored

(2) There are five sets of nitrogen configurations for a coplanar array of nitrogen donors. Schematically these are

B + +   D + −
+ +   + −
C − +   E + +
+ −   + −
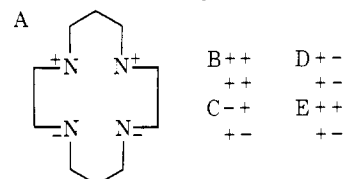
Discussions of stereochemistry in these systems of a general nature are given by B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102 (1965). A more detailed analysis is given by L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 4092 (1969); "Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, Jr.," Plenum Press, New York, N. Y., 1969. The trans-dichloro complex of **2** has the set of nitrogen configurations shown as (A): B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(3) G. W. Watt and P. W. Alexander, *Inorg. Chem.*, 7, 537 (1968), and references cited.

(4) W. L. Jolly, *Inorg. Syn.*, 11, 113 (1968); *J. Chem. Educ.*, 44, 304 (1967).

(5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 84, 866 (1962); 87, 1345 (1965).