OPEN SHELL CNDO TREATMENTS
ON SMALL INORGANIC RADICALS

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The configuration interaction treatment, based on the molecular orbitals given by the open shell SCF procedure of Longuet-Higgins and Pople within the framework of the CNDO version of Del Bene and Jaffé, has been employed to interpret the electronic spectra, ionization potentials, and electron affinities of radicals containing 2, 3, and 4 atoms. Considering the feasibility and small cost involved, the procedure seems to be very useful. With the HO_2 radical the theory predicts a transition, not yet observed either in the near infrared or at the beginning of the visible region. The molecular geometries predicted by means of the CNDO/2 method are of comparable accuracy to those obtained by standard closed shell treatments.

In an earlier paper[1] we reported the results of CNDO calculations on the electronic spectra and some ground state properties of BH_2, NH_2, HCO, NO_2, NF_2, HNCN, BOF_2, H_2NO, and CH_2N radicals. The present paper extends this study to BeH, BH^+, BO, CN, CO^+, N_2^+, HNF, HO_2, FO_2, FCO, and F_2CN radicals.

DESCRIPTION OF THE CALCULATIONS

The calculations undertaken were of the CNDO type making use of the open shell method of Longuet-Higgins and Pople[2] (LHP). Estimations of molecular geometries and dipole moments were based on the standard CNDO/2 scheme[3]. For a theoretical approach to ionization potentials, electron affinities, and electronic spectra we have used the Del Bene and Jaffé procedure[4] hereafter referred to as DBJ (SCF part only) or DBJ-LCI (configuration interaction included). All of the approximations involved and the semiempirical parameters used are those given in the original publications[3,4]. The only modification adopted concerns the two center repulsion integrals in the DBJ scheme, where we use the Mataga–Nishimoto approximation rather than that of Pariser and Parr. By considering the trends in the CNDO/2 and DBJ parameters for hydrogen, carbon, nitrogen, and oxygen we tentatively chose for boron and fluorine the following parameters in the DBJ computational scheme: $\gamma_{BB} = 10\cdot2$ eV; $\beta_B^0 = -15$; $\gamma_{FF} = 13\cdot9$ eV; $\beta_F^0 = -55$. For berylium we have not derived DBJ parameters because in BeH there is no $p - p$ overlap, hence the CNDO/2 method can be expected to give reasonable results for the ground state properties as well as for electronic spectra and ionization potentials. Actually, we have found for BH_2 and NH_2 that the respective differences between the CNDO/2 and DBJ results

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are very small[1]. Equilibrium molecular configurations were calculated by automatic minimization of energy[5], otherwise the experimental molecular geometries were used. The latter are listed together with the references in Table I; for HO_2 we assume the bond angle 110°. In the configuration interaction treatment we have considered 10—50 singly excited states depending on the size of the molecule. By adopting the approximations involved in Koopmans theorem, the first ionization potential and the first electron affinity can be expressed in the framework of the LHP method as follows[6]:

$$-I = \varepsilon_m - \tfrac{1}{2}J_{mm}, \qquad (1)$$

$$-A = \varepsilon_m + \tfrac{1}{2}J_{mm}, \qquad (2)$$

where ε_m and J_{mm} are the orbital energy and Coulomb repulsion integral for the singly occupied molecular orbital m. A more detailed description of the computational method is given elsewhere[6].

RESULTS AND DISCUSSION

Ground state properties. Table I presents the equilibrium bond lengths and bond angles calculated by the CNDO/2-LHP method. These results are compared with the

TABLE I

Calculated and Experimental Bond Lengths (Å) and Bond Angles

System	R_{XY}	CNDO/2[a]	INDO[b]	Expt.[c]	ϑ	CNDO/2[a]	INDO[b]	Expt.
BeH	Be—H	1·310	—	1·3431	—	—	—	—
BH$^+$	B—H	1·169	—	1·2146				
BO	B—O	1·279	—	1·2049	—	—	—	—
CN	C—N	1·153	—	1·1718				
CO$^+$	C—O	1·161	—	1·1151	—	—	—	—
N$_2^+$	N—N	1·112	—	1·1162				
HNF	H—N	1·063	1·08	1·026[d]	⋊ HNF	108	106·4	105[d]
	N—F	1·204	1·23	1·400[d]				
HO$_2$	H—O	1·031	1·05	0·958[e]	⋊ HOO	111	110·7	105 ± 5[e]
	O—O	1·165	1·19	1·30[e]				
FO$_2$	F—O	1·195	1·19	1·575[f]	⋊ FOO	112	110·6	109·5[f]
	O—O	1·220	1·19	1·217[f]				
FCO	F—C	1·300	1·32	1·34[g]	⋊ FCO	131	129·4	135[g]
	C—O	1·216	1·23	1·18[g]				
F$_2$CN	F—C	1·324	1·33	1·31[h]	⋊ FCF	107	108·6	113·5[i]
	C—N	1·248	1·28	1·265[i]				

[a] LHP method used; [b] ref.[7], the UHF method used; [c] Taken from ref.[8] unless otherwise stated; [d] Based on estimations[9]; [e] ref.[10], bond lengths assumed; [f] In analogy[11] with F_2O_2; [g] Based on estimations[12]; [h] Assumed[13]; [i] ref.[13].

experimental data on the one hand, and with the calculated data[7] obtained by the unrestricted INDO method on the other. It can be seen that the two open shell methods yield results which are in remarkable agreement. The quality of the agreement between the calculated and observed data is similar to that found in INDO treatments on closed shell systems[7]. Even the trends in deviations appear to be similar, *e.g.* also here the theory underestimates drastically the O—O, N—F and O—F bond lengths. For the sake of comparison we present here results of recent *ab initio* calculations for CN (ref.[14]), HO_2 (ref.[15]) and FO_2 (ref.[16]): $r(CN) = 1.236$ Å, $r(OH) = 0.968$ Å, $r(OO) = 1.384$ Å, $\sphericalangle$ HOO = 106·8°, with FO_2 the unsymmetrical structure is favoured over the symmetrical one.

Table II comprises data on ionization potentials, electron affinities, and dipole moments. The average error in the predicted ionization potentials and electron affinities is 0·8 eV, which is comparable with the accuracy achieved with the closed shell DBJ calculations[21,22].

For chemical purposes we present in Fig. 1 molecular diagrams involving atomic net charges, Wiberg bond indices[23], and electron distributions in singly occupied molecular orbitals.

Electronic spectra. DBJ–LCI and experimental spectral data are summarized in Table III. With diatomic systems the results can be characterized as rather satisfactory for BeH, BH^+, BO and CO^+. With CN the theory reproduces qualitatively the nature of the spectrum but underestimates the first transition energy. This is the

TABLE II
Ionization Potentials, Electron Affinities and Dipole Moments

System	I^a	A^a	μ^b
BeH	9·44	−0·16	0·692
BH^+	20·87	11·49 (9·77 ± 0·05)	—
BO	12·24	3·08	1·234
CN	13·09 (14·2 ± 0·3)	4·35 (3·7 ± 0·2)^c	0·770
CO^+	23·54	14·22 (14·01)	—
N_2^+	24·06	14·94 (15·6)	—
HNF	12·47	1·43	1·924
HO_2	11·90 (11·53 ± 0·02)	1·52 (3·04)^d	2·238
FO_2	12·19 (12·6 ± 0·2)	1·91	0·650
FCO	10·35	1·93 (2·7)^e	0·327
F_2CN	11·84	0·42	1·318

^{a} DBJ data (except for BeH, see text) in eV, experimental data (in parentheses) taken from ref.[17] unless otherwise stated; ^{b} CNDO/2 data in Debye units; ^{c} Ref.[18]; ^{d} Ref.[19]; ^{e} Ref.[20].

case also with N_2^+, where the LCI treatment even gives a $^2\Pi_u$ state of lower energy than the $^2\Sigma_g^+$ (SCF ground) state. Fig. 2 presents the result of the investigation into whether or not this is due to the bond length employed. It can be seen that any change in the bond length in CN within the region considered leaves the picture qualitatively unchanged. With N_2^+ the agreement between theory and experiment is even less satisfactory. Recently two *ab initio* studies on CO^+, N_2^+ and CN have appeared[14,30]. The former[30] concerns the $^2\Pi$ and $^2\Delta$ states only, the results of the latter[14] are indicated in Fig. 2.

The CNDO/2 calculation for HNF yields the same order of orbital levels as that given by the Walsh diagram[31]:

$$(1a')^2 (2a')^2 (3a')^2 (1a'')^2 (4a')^2 (5a')^2 (2a'')^1$$

FIG. 1

Atomic Net Charges, Wiberg Bond Indices and Electron Distributions in Singly Occupied Molecular Orbitals (in parentheses)

All entries are based on the CNDO/2 calculations using experimental molecular geometries.

FIG. 2

DBJ–LCI Transition Energies in CN and N_2^+ as a Function of the Bond Length

Observed transition energies[8,29] are indicated by horizontal lines. Experimental bond lengths are indicated by arrows, the results of recent *ab initio* calculations[14] by dots.

TABLE III
Electronic Spectra[a]

System	$\tilde{\nu}_1$	$\log f_1$	Assignment	$\tilde{\nu}_2$	$\log f_2$	Assignment	$\tilde{\nu}_3$	$\log f_3$	Assignment
BeH calc.[b]	16·20	−1·19	$^2\Pi \leftarrow {}^2\Sigma^+$	60·58	−1·17	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$	70·50	−1·22	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$
obs.[c,d]	20·03								
BH⁺ calc.[c]	21·98	−1·46	$^2\Pi \leftarrow {}^2\Sigma^+$	70·55	−1·22	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$	—	—	—
obs.[c]	26·38								
BO calc.[e]	34·74	−1·80	$^2\Pi \leftarrow {}^2\Sigma^+$	39·98	−1·29	$^2\Pi \leftarrow {}^2\Sigma^+$	50·95	−1·53	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$
obs.[e,f]	23·90[e,f]						43·17		
CN calc.[e]	1·48	−3·30	$^2\Pi \leftarrow {}^2\Sigma^+$	32·27	−1·21	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$	38·14	−2·42	$^2\Pi \leftarrow {}^2\Sigma^+$
obs.[e]	9·24			25·75					
CO⁺ calc.[c]	16·58	−2·25	$^2\Pi \leftarrow {}^2\Sigma^+$	44·86	−1·25	$^2\Sigma^+ \leftarrow {}^2\Sigma^+$	49·95	−1·67	$^2\Pi \leftarrow {}^2\Sigma^+$
obs.[c]	20·73			45·88					
HNF calc.[g]	25·24	−2·11	$^2A' \leftarrow {}^2A''$	73·39	−2·16	$^2A'' \leftarrow {}^2A''$	75·86	−1·50	$^2A'' \leftarrow {}^2A''$
obs.[g]	20·00—25·64								
HO₂ calc.[h]	3·12	forb.	$^2A' \leftarrow {}^2A''$	62·48	−0·88	$^2A'' \leftarrow {}^2A''$	64·71	−2·00	$^2A' \leftarrow {}^2A'$
obs.[h]				34·5—51·3					
FO₂ calc.[i]	9·90	forb.	$^2A' \leftarrow {}^2A'$	47·05	−2·77	$^2A' \leftarrow {}^2A'$	66·08	−1·18	$^2A'' \leftarrow {}^2A''$
obs.[j]	16·7—18·2	$\varepsilon < 100$		>33					
FCO calc.	15·05	−2·40	$^2A'' \leftarrow {}^2A'$	35·75	−2·60	$^2A' \leftarrow {}^2A'$	37·10	−1·56	$^2A' \leftarrow {}^2A'$
obs.	18·55[k]						29·4—45·5[l]		
F₂CN calc.[m]	36·15	−2·02	$^2A_1 \leftarrow {}^2B_2$	26·35	forb.	$^2B_1 \leftarrow {}^2B_2$	26·58	forb.	$^2B_2 \leftarrow {}^2B_2$
				52·03	−1·65	$^2A_2 \leftarrow {}^2B_2$	52·36	−2·11	$^2A_2 \leftarrow {}^2B_2$
obs.[n,o]	27·6—29·5								

[a] $\tilde{\nu}$ and f stand for wavenumbers (10^{-3} cm^{-1}) and oscillator strengths; [b] CNDO/2-LCI calculations, see text; [c] Emission[8], [d] The next $^2\Pi \leftarrow {}^2\Sigma^+$ band observed at 50 934 cm^{-1} is due to a Rydberg transition[24]; [e] Both emission and absorption[8], [f] Average value; [g] ref.[9]; [h] ref.[25], [i] In the most recent papers the reported absorption maximum in the gas phase is located at 47 700 cm^{-1} (ref.[34]) and 48 800 cm^{-1} (ref.[35]); [j] Near the allowed transition at 64 700 cm^{-1} there is a forbidden transition at 66 080 cm^{-1} ref.[27]; [k] ref.[26], [l] ref.[27], [m] the values for $\tilde{\nu}_4$ ($\log f_4$), $\tilde{\nu}_5$($\log f_5$) and $\tilde{\nu}_6$($\log f_6$); [n] ref.[13], the MO calculation reported in that paper also gives the $^2B_2$ ground state; [o] ref.[28]
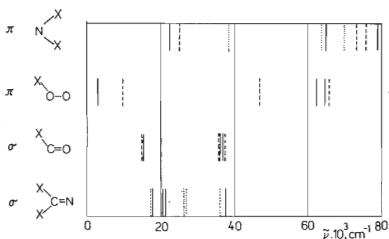
FIG. 3

Effect of Fluorine Substitution on the Electronic Spectra

Full, dashed and dotted lines represent DBJ–LCI transition energies for unsubstituted, monofluoro and difluoro derivatives. Types of radicals (σ or π) are indicated on the formulas.

whereas in the DBJ scheme the order of the 1a″ and 4a′ levels is interchanged. The energy differences between the critical orbitals are, however, very small in both SCF approaches. From the two candidates considered for the lowest excited state[31] the DBJ–LCI calculation favours that having the... $(5a')^1 (2a'')^2$ configuration, the first band being interpreted well. One can expect on theoretical grounds the next band to appear in the vacuum UV region.

The literature data on HO_2 are rather incomplete. Walsh[32] concludes that the HO_2 radical should have at least one allowed low-lying electronic transition, $^2A' \leftarrow {}^2A''$, polarized perpendicularly to the molecular plane. Our calculation supports this conclusion giving a transition with a non-vanishing transition moment (0.01) perpendicular to the molecular plane. The predicted transition energy, $3100\ cm^{-1}$, should be taken with some caution, nevertheless one can expect a band in the long-wavelength region. The theory overestimates the transition energy for the band in the UV region[25,27,33–35], however the situation is somewhat uncertain due to the reported fact that HO_2 undergoes photolysis[36] at $\lambda < 220$ nm.

With FO_2 the theory predicts two transitions at 9900 and $47050\ cm^{-1}$ and therefore it appears that the small maximum observed[26] at $23000\ cm^{-1}$ could be due to the absorption of a dimer or some other species. The electronic spectrum of FCO is interpreted well. The theory suggests that the broad band in the UV region is due to two transitions. Good agreement is also found with F_2CN. Here one can expect, on the basis of calculations, further weak bands in the longer wavelength region.

An interesting effect of fluorine substitution is visualized in Fig. 3. With the π radicals studied fluorine substitution causes a considerable hypsochromic shift of their first bands, whereas with σ radicals the spectra remain almost unchanged. Finally

let us add that with all of the radicals under study the three lowest excited states are represented by nearly pure electronic transitions, the weights of main configurations in the upper states being over 80 per cent.

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