The Electronic Structures of NO_2, NO_2^+ and NO_2^-

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Several quantum-mechanical investigations have been carried out on the electronic structures of NO_2,[1,2,3] NO_2^+,[1,4,5] and NO_2^-.[1] That is, Walsh[1] discussed the electronic structure of these molecules by qualitative considerations. Tanaka[2] and McEwen[3] treated the π electronic structure of NO_2 by the LCAO SCF method, and, further, McEwen investigated the σ non-bonding electrons by the semi-emprical method.

On the other hand, the present authors and others have developed the Hückel molecular orbital treatment of saturated compounds and also the σ electronic structure of unsaturated compounds.[6] Hoffmann has recently proposed an extended Hückel molecular orbital method in which σ and π electronic structures of saturated and unsaturated hydrocarbons are treated simultaneously.[7]

In the present paper, the electronic structures of NO_2, NO_2^+ and NO_2^- will be calculated by Hoffmann's method, and some physico-chemical properties of these compounds will be discussed.

Method of Calculation

By Hoffmann's method the molecular orbitals (MO) of these compounds are represented by the linear combination of valency atomic orbitals (AO), that is, the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of the nitrogen and oxygen atoms. Therefore, the secular determinant is given by

$$\det |H_{ij}-ES_{ij}|=0$$

whers H_{ij} is the off-diagonal element and S_{ij} is the overlap integral between the ith and jth atomic orbitals. The values of the diagonal elements, H_{ii}, are given with reference to those given by Skinner and Pritchard[8]:

$$H(2\text{s, N})=-27.5\text{ eV.}\quad H(2\text{p, N})=-14.5\text{ eV.}$$

$$H(2\text{s, O})=-35.3\text{ eV.}\quad H(2\text{p, O})=-17.8\text{ eV.}$$

and the off-diagonal element, H_{ij}, is expressed as:

$$H_{ij}=0.5K(H_{ij}+H_{ji})S_{ij}$$

where the value of K is taken as 1.75, as in Hoffmann's paper,[7] and the values of S_{ij} are

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[1] A. D. Walsh, *J. Chem. Soc.*, **1953**, 2266.

[2] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1643 (1957).

[3] K. L. McEwen, *J. Chem. Phys.*, **32**, 1801 (1961).

[4] S. Nagakura and J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 993 (1954).

[5] E. Clementi and A. D. McLean, *J. Chem. Phys.*, **39**, 323 (1963).

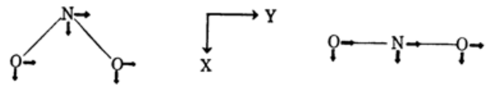
[6] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 442, 1111, 1814 (1961); K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, ibid., **35**, 38 (1962); K. Morokuma, K. Fukui, T. Yonezawa and H. Kato, ibid., **36**, 47 (1963).

[7] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); ibid., **40**, 2474, 2480, 2745 (1964).

[8] H. A. Skinner and H. O. Pritchard, *Chem. Revs.*, **55**, 745 (1955).

obtained by Mulliken's Table.[9]

The shapes of these molecules are given as follows:[10] The N–O distance is 1.15 Å for NO_2^+, 1.20 Å for NO_2, and 1.235 Å for NO_2^-, and the angle of ONO is 180° for NO_2^+, 132° for NO_2, and 115° for NO_2^-. Thus, NO_2 and NO_2^- belong to the point group C_{2v}, and NO_2^+ belong to the group $D_{\infty h}$. The coordinate is taken as shown in Fig. 1, where the p_z orbitals are perpendicular to the XY plane.



NO_2, NO_2^- NO_2^+

Fig. 1. The coordinates and the directions of p_x, p_y orbitals.

Results and Discussion

Electronic Levels and Distributions.—The calculated MO energies (in eV.) and the values of the coefficients of AO's in some MOs are listed in Table I (a), (b) and (c), together with the irreducible representations of each MO. From the results listed in Table I, the following facts can be deduced: In NO_2^+, the highest occupied orbital (HO) consists of the π orbitals of the oxygen atoms, the odd electron in NO_2 is mainly localized on the lone-pair orbital of the nitrogen atom, and a

TABLE I. (a) MOLECULAR ORBITALS OF NO_2^+

Irreducible representation	Orbital energy, eV.	Molecular orbital***
e_{1u}*	−10.88	$0.953Z_N-0.484(Z_O+Z_O')$
e_{1u}*	−10.88	$0.953X_N-0.484(X_O+X_O')$
e_{1g}**	−17.72	$0.710(X_O-X_O')$
e_{1g}**	−17.72	$0.710(Z_O-Z_O')$
a_{2u}	−18.75	$-0.251Y_N-0.135(S_O-S_O')+0.621(Y_O+Y_O')$
e_{1u}	−19.28	$0.428Z_N+0.556(Z_O+Z_O')$
e_{1u}	−19.28	$0.428X_N+0.556(X_O+X_O')$

* The lowest vacant orbitals (degenerated)

** The highest occupied orbitals (degenerated)

*** The notations S_N, X_N, Y_N and Z_N denote the 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of the nitrogen atom and the prime is used to represent the orbitals of the second oxygen atom.

TABLE I. (b) MOLECULAR ORBITALS OF NO_2

Irreducible representation	Orbital energy, eV.	Molecular orbital***
b_1*	−11.58	$0.949Z_N-0.454(Z_O+Z_O')$
a_1**	−13.19	$0.319S_N-0.802X_N-0.022(S_O+S_O')-0.037(Y_O-Y_O')+0.487(X_O+X_O')$
b_2	−17.46	$-0.061Y_N-0.005(S_O-S_O')+0.472(Y_O+Y_O')+0.537(X_O-X_O')$
a_2	−17.69	$0.710(Z_O-Z_O')$
b_2	−18.85	$0.275Y_N+0.131(S_O-S_O')-0.426(Y_O+Y_O')+0.416(X_O-X_O')$
a_1	−18.98	$-0.060S_N+0.368X_N-0.061(S_O+S_O')+0.366(Y_O-Y_O')+0.461(X_O+X_O')$
b_1	−19.11	$0.414Z_N+0.570(Z_O+Z_O')$

* The lowest vacant orbital. ** The odd electron orbital.

TABLE I. (c) MOLECULAR ORBITALS OF NO_2^-

Irreducible representation	Orbital energy, eV.	Molecular orbital***
b_1*	−11.91	$0.948Z_N-0.437(Z_O+Z_O')$
a_1**	−14.24	$0.355S_N-0.736X_N-0.011(S_O+S_O')-0.016(Y_O-Y_O')+0.491(X_O+X_O')$
b_2	−17.18	$-0.082Y_N+0.006(S_O-S_O')+0.576(Y_O-Y_O')+0.491(X_O+X_O')$
a_2	−17.65	$0.711(Z_O-Z_O')$
b_2	−18.88	$0.294Y_N+0.124(S_O-S_O')-0.345(Y_O+Y_O')+0.501(X_O-X_O')$
a_1	−18.89	$-0.080S_N+0.327X_N-0.072(S_O+S_O')+0.426(Y_O-Y_O')+0.390(X_O+X_O')$
b_1	−19.04	$0.404Z_N+0.578(Z_O+Z_O')$

* The lowest vacant orbital. ** The highest occupied orbital.

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[9] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[10] A. D. Mitchell, L. C. Cross et al., "Table of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).

TABLE II. THE TYPES OF TRANSITION AND THE CALCULATED AND OBSERVED TRANSITION ENERGIES OF NO_2 (eV.)

	Type of transition by Walsh	Calcd. eV.	Obs. eV.
from	$-(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_2)^2(a_1)$		
to	$-(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_2)^2(b_1)$	1.61	1.36～3.87
	$-(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_2)(a_1)^2$	4.27	
	$-(b_1)^2(a_1)^2(b_2)^2(a_2)(b_2)^2(a_1)^2$	4.50*	
	$-(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_2)(a_1)(b_1)$	5.88*	
	$-(b_1)^2(a_1)^2(b_2)^2(a_2)(b_2)^2(a_1)(b_1)$	6.11	4.77～5.46
	$-(b_1)^2(a_1)^2(b_2)(a_2)^2(b_2)^2(a_1)^2$	5.66	
	$-(b_1)^2(a_1)(b_2)^2(a_2)^2(b_2)^2(a_1)^2$	5.80	7.75～9.18
	$-(b_1)(a_1)^2(b_2)^2(a_2)^2(b_2)^2(a_1)^2$	5.92	

* Forbidden transitions

similar tendency is observed in the HO of NO_2^-. The lowest orbitals (LV) of these compounds are all π anti-bonding orbitals, largely localized on the nitrogen atom. The order of our calculated orbitals of NO_2 and NO_2^- are consistent with the results estimated by Walsh[1],* and that of NO_2^+, with the results of Clementi and McLean.[5]

The energy of LV of NO_2^+ was estimated as -11 eV. by Nagakura and Tanaka[4]; the present result is -10.88 eV. The energy of the HO of NO_2 is calculated as -13.19 eV., while the value obtained by McEwen was -13.21 eV. The observed ionization energy is 13.98[11] or 11.7 eV[12],**. The π orbital energies of NO_2 obtained by the present calculations are -19.11, -17.69 and -11.58 eV., while by the LCAO SCF method, Tanaka[2] computed -18.86, -15.63 and $+0.40$ eV. and McEwen obtained -19.18, -15.85 and -2.23 eV..

The electronic distributions of the above-mentioned results, however, are considerably different. That is, the magnitudes of the π electron densities obtained by Tanaka are 1.018 on the nitrogen atom and 1.491 on the oxygen atom, whereas the values obtained by McEwen are 0.728 on the nitrogen atom and 1.637 on the oxygen atom in NO_2. In our calculations, the values of the atomic populations[13] of π electrons are 0.516 on the nitrogen atom and 1.742 on the oxygen atom in this molecule. For the odd electron distributions, the values by McEwen are 0.364 on the nitrogen atom and 0.318 on the oxygen atom, while our calculated atomic populations are 0.630 on the nitrogen atom and 0.158 on the oxygen atom. The net charges by our calculations are $+1.68$ on the nitrogen atom and -0.84 on the oxyen atom (considering all valence electrons), whereas Tanaka estimated the net charges to be $+0.88$ on the nitrogen atom and -0.44 on the oxygen atom (including σ and π electrons). Our calculated negative charge of the oxygen atom, however, seems to be too large. Although this might partly arise from the oozing of nitrogen lone-pairs, the difference in electronegativity between nitrogen and oxygen atoms might be overestimated to a certain extent in the present treatment.

Reactivity.—As has been described in the section on electronic levels, the highest occupied orbitals of NO_2 and NO_2^- are the lone-pair orbitals, in which the bonding electrons are largely localized on the nitrogen atom.*** Accordingly, by our frontier electron theory, the radical reaction of NO_2 will more likely take place at the nitrogen atom than at the oxygen atom. This theory may be supported by the following experimental facts: The hydrogen atom abstraction reaction by NO_2 produces $H:NO_2$,[1] and the structure of N_2O_4, produced by the association of NO_2, is regarded as $O_2N:NO_2$ rather than $ONO:NO_2$.[14] The structure of N_2O_3 produced from NO and NO_2 is represented by $ON:NO_2$.[14] Also, the NO_2^- ion mostly reacts with alkyl ions to form a nitro-compounds.[1] Considering the values of the coefficients of the AO's of the HO orbital in NO_2 and NO_2^-, the reaction described above may occur partly at the oxygen atoms, corresponding to the experience in the reaction of alkyl compounds with NO_2 producing the nitrous esters as by-products.[15]

Similarly, for the NO_2^+ cation, the "nucleophilic" reaction will take place on the nitrogen atom (for instance, as in the "electrophilic" nitration of aromatic hydrocarbons), and it may be predicted that the electrophilic reaction

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* McEwen assumed a different order in NO_2, that is, $-(b_1)^2(a_2)^2(a_1)^2(b_2)^2(a_1)$. (cf. Table II.)

** The calculated energy of the HO of NO_2^- seems to be too low. This discrepancy might be partly attributed to the disregard of the change in Coulomb integrals in the ionized state.

*** The Lone-pair orbital of the nitrogen atom is directed towards $(-X)$. This may have some relation with its orientation as a nitrating reagent.

[11] J. Collin and F. P. Lossing, *J. Chem. Phys.*, **28**, 900 (1958).

[12] K. Watanabe, ibid., **26**, 542 (1957).

[13] R. S. Mulliken, ibid., **23**, 1833 (1955).

[14] See, e. g., R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," Elsevier Pub. Co., London (1960).

[15] See, e. g., B. T. Brooks, C. E. Boord et al., "The Chemistry of Petroleum Hydrocarbons," Reinhold Pub., N. Y. (1954).

will occur on the oxygen atoms.

Transition Energy. — Walsh discussed in detail the ultraviolet spectroscopic data of NO_2 in connection with the type of transition.[1] The types of transition estimated by Walsh and the calculated energy differences are summarized in Table II, together with the observed absorptions. Except for the transition to the highest vacant a_1 orbital,* the calculated values agree well with the observed values. On the other hand, the π-π transition energies computed by Tanaka[2] are 8.30 and 7.53 eV, while our calculated values are 7.36 and 6.11 eV.

As has been mentioned above, the calculated results have a good correlation with the experimental values and other calculations, though there are a few discrepancies. The discrepancy of the electron distribution can be modified by the ω-technique[16] or by using larger values of the parameter K (in particular for π-π bonding). This point will be published in the near future.

A part of the calculations have been carried out on the digital computer, KDC-I, of Kyoto University.

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* The calculated energy of the highest vacant a_1 orbital is +18.19 eV.

[16] G. W. Wheland and D. E. Mann, *J. Chem., Phys.*, **17**, 264 (1949).