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Molecular Orbital Treatment of Nitric Oxide Radicals. I. Electronic Structure and Spectrum of the H_2NO Radical

Osamu KIKUCHI

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

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A theoretical treatment of the H_2NO radical is presented. In the calculation, the approximate SCF method of Longuet-Higgins and Pople for open-shell molecules is applied to the valence electron system, the CNDO/2 approximation is adopted, and the molecular excited states are approximated by linear combinations of some doublet Slater determinants constructed by means of the SCF MO for the ground state. The results thus obtained for the electronic structure of the H_2NO radical are discussed. The calculated spectrum for the H_2NO radical shows that the longest wavelength band has the $n\rightarrow\pi^*$ character, and the $\pi\rightarrow\pi^*$ transition energy is smaller than that for the $n\rightarrow\sigma^*$ transition. The $\pi\rightarrow\pi^*$ transition energy, 5.77 eV, calculated by the method in which only the π-electrons were explicitly considered, indicated that the $\pi\rightarrow\pi^*$ band falls into the area near 240 mμ. From the calculated results for the H_2NO radical and the solvent effect on the absorption bands of aliphatic nitric oxide radicals, two bands, at 450 mμ, and 240 mμ, characteristic of the latter radicals have been assigned to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions respectively.

Nitric oxide radicals are among the most typical organic radicals and have been widely investigated by maens of the ESR method.[1,2] Briere, Lemaire, and Rassat have studied the electronic structures of various stable nitric oxide radicals by the IR, UV, and ESR methods.[2] They have synthesized some aliphatic nitric oxide radicals and measured their electronic absorption spectra and ESR spectra; they found that two electronic absorption bands appear, at 450 mμ and 240 mμ, and that the nitrogen hyperfine splitting constant and the g value are 15—16 gauss and 2.0055 respectively. Since, in these nitric oxide radicals, an odd electron is almost completely localized on the $2p\pi$ orbitals of nitrogen and oxygen, the above characteristic properties can be expected to be understood on the basis of the electronic structure of the N–O group.

In theoretical treatment attempting to determine the electronic structure of open-shell systems such as aliphatic nitric oxide radicals, it is necessary to treat not only π-electrons, but also σ-electrons at the same time. An approximate method to obtain the LCAO-SCF-MO for the π-electron system of open-shell molecules was proposed by Longuet-Higgins and Pople[3] and was later applied to a theoretical treatment of the π-electronic structures of organic radicals.[4] An approximate method for obtaining SCF molecular orbitals for all valence electrons in closed-shell molecules was presented by Pople, Santry, and Segal.[5] They found that completely neglecting the differential overlap (CNDO) approximation in electron-repulsion integrals leads to results which are invariant to simple transformations of the atomic orbital basis set when these integrals satisfy a further restrictive relationship. This approximate method with CNDO was later modified in some ways; the new method was denoted the "CNDO/2 approximation".[5] They used this CNDO/2 method to calculate molecular orbitals for the valence electrons of some closed-shell molecules and have obtained reasonable theoretical results for some electronic properties of molecules.[5]

As the first step of the molecular orbital treatment of nitric oxide radicals, the present investigation intends to obtain information about the electronic

1) Y. Deguchi, This Bulletin, **34**, 910 (1961); J. Pannell, *Mol. Phys.*, **7**, 317 (1964); J. Yamauchi, H. Nishiguchi, K. Mukai, Y. Deguchi and H. Takaki, This Bulletin, **40**, 2512 (1967); A. L. Buchachenko, *Akad. Nauk S. S. S. R.*, **6**, 1120 (1963); G. Chapelet-Letourneux, H. Lemaire, A. Rassat and J. P. Ravet, *Bull. Soc. Chim. France*, **1965**, 1975; O. Kikuchi and K. Someno, This Bulletin, **40**, 2549 (1967); A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961); N. B. Neiman, E. G. Rozanzev and Yu. G. Mamedova, *Nature*, **196**, 476 (1963).

2) R. Briere, H. Lemaire and A. Rassat, *Bull. Soc. Chim. France*, **1965**, 3273.

3) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **68**, 591 (1955).

4) A. Ishitani and S. Nagakura, *Theoret. Chim. Acta (Berl.)*, **4**, 236 (1966).

5) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

structure of aliphatic nitric oxide radicals and to assign the two characteristic absorption bands at 450 mμ and 240 mμ. For this purpose, we will use the H_2NO radical, which is the simplest nitric oxide radical and the ESR spectrum of which has been obtained.[6] The approximate SCF method of Longuet-Higgins and Pople will be applied to the valence electron system with the CNDO/2 approximation, and the electronic structure and spectrum of the H_2NO radical will be discussed.

Theoretical

The Hamiltonian operator, $\mathcal{H}$, is expressed in the form:

$$\mathcal{H} = \sum_i H_{\text{core}}(i) + \sum_{i>j} e^2/r_{ij} \tag{1}$$

where $H_{core}(i)$ is the sum of the kinetic energy operator for the valence electron, i (the 1s electron for hydrogen and the 2s and 2p electrons for carbon, nitrogen, and oxygen atoms), and the potential energy operator in the core field (nucleus and inner electrons).

The ground configuration of the free radical is doublet, and its antisymmetrized wave function is described by:

$$\Psi_g = |\, \phi_1\bar{\phi}_1 \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m \,| \tag{2}$$

where the number of valence electrons is $2m-1$. The excited doublet configurations considered are of the following four types:

$$\left.\begin{aligned}
\Psi_{m\to k} &= |\, \phi_1\bar{\phi}_1 \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_k \,| \\
\Psi_{i\to m} &= |\, \phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_m \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m \,| \\
\Psi_{i\to k}(\mathrm{I}) &= \frac{1}{\sqrt{2}}\{|\, \phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_k \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m \,| \\
&\quad + |\, \phi_1\bar{\phi}_1 \cdots \phi_k\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m \,|\} \\
\Psi_{i\to k}(\mathrm{II}) &= \frac{1}{\sqrt{6}}\{|\, \phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_k \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m \,| \\
&\quad - |\, \phi_1\bar{\phi}_1 \cdots \phi_k\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m| \,\} \\
&\quad - 2|\, \phi_1\bar{\phi}_1 \cdots \phi_i\phi_k \cdots \phi_{m-1}\bar{\phi}_{m-1}\bar{\phi}_m \,|
\end{aligned}\right\} \tag{3}$$

where i and k are labeled as the doubly-occupied and the unoccupied orbitals respectively in the ground configuration. In the present treatment, the electronic wave functions for ground and excited doublet states are approximated by linear combinations of the above configurations:

$$\Phi = \sum_i A_i\Psi_i \tag{4}$$

For the open-shell molecules, an approximate method for obtaining self-consistent molecular orbitals for π-electrons was proposed by Longuet-Higgins and Pople.[3] We applied their method to the valence electron system using the CNDO/2 approximation. The valence electrons are assigned to LCAO molecular orbitals:

$$\phi_i = \sum_r C_{ri}\chi_r \tag{5}$$

where χ_r are valence atomic orbitals. The molecular orbital energies and LCAO coefficients are obtained by:

$$\sum_s (F_{rs}-\delta_{rs}\varepsilon)C_{si} = 0 \tag{6}$$

and the matrix elements are given by:

$$\left.\begin{aligned}
F_{rr} &= U_{rr} + \left(P_{AA}-\frac{1}{2}P_{rr}\right)\gamma_{AA} + \sum_{B(\neq A)}(P_{BB}-\zeta_B)\gamma_{AB} \\
F_{rs} &= \frac{1}{2}(\beta_A + \beta_B)S_{rs} - \frac{1}{2}P_{rs}\gamma_{AB} \quad (r \neq s)
\end{aligned}\right\} \tag{7}$$

where the electron-density and bond-order matrix, P_{rs}, is given by:

$$P_{rs} = \sum_{i=1}^{m-1} 2C_{ri}C_{si} + C_{rm}C_{sm} \tag{8}$$

and where the other notations are the same as those given by Pople *et al.*[5] The choice of all the parameters except the bonding parameters are entirely based on them; the bonding parameters, β_A, are determined by the method to be described in the next section.

An initial calculation of the molecular orbital coefficients is carried out by a Hückel-type calculation; iterations are then performed until self-consistency is achieved on all orbital energies with a tolerance of 0.00005 eV. All the present calculations were carried out with the HIPAC 103 computer of Tokyo Kyoiku University.

Results and Discussion

At first the values of bonding parameters, β_A, were reexamined. Pople *et al.* have determined the values of bonding parameters empirically so that the CNDO calculations give the best over-all fit with the accurate LCAO-SCF calculations on diatomic molecules.[5] For the orbital energy intervals, the bonding parameters listed in their article reproduce almost well those obtained by the full LCAO-SCF calculations. However their results also show that the orbital energy intervals $(\varepsilon_j-\varepsilon_i)$ are not satisfactory for π-orbitals; the discrepancy from the results obtained by the full LCAO-SCF calculations is about 3.5 eV for some diatomic molecules. Therefore, their values will not be the best ones to discuss all the kinds of electronic transitions, such as $n\to\pi^*$, $n\to\sigma^*$, and $\pi\to\pi^*$, at the same time. To obtain bonding parameters appropriate to the present calculations, the formaldehyde molecule was chosen as an example; for it the $n\to\pi^*$, $n\to\sigma^*$, and $\pi\to\pi^*$

6) C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, **1965**, 751; J. Q. Adams, S. W. Nicksic and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

TABLE 1. LCAO SCF MO'S OF FORMALDEHYDE*1

MO	Orbital energy (eV)	Symmetry	Coefficients									
			1s(H_1)	1s(H_2)	2s(C)	2p_x(C)	2p_y(C)	2p_z(C)	2s(O)	2p_x(O)	2p_y(O)	2p_z(O)
ϕ_1	−39.96	a_1	0.1258	0.1258	0.4357	0.0000	0.2643	0.0000	0.8352	0.0000	−0.1055	0.0000
ϕ_2	−26.67	a_1	0.3782	0.3782	0.6222	0.0000	−0.2666	0.0000	−0.3941	0.0000	−0.3167	0.0000
ϕ_3	−22.46	b_2	0.3403	−0.3403	0.0000	0.5828	0.0000	0.0000	0.0000	0.6548	0.0000	0.0000
ϕ_4	−18.48	a_1	0.2334	0.2334	−0.0248	0.0000	−0.5692	0.0000	0.2140	0.0000	0.7216	0.0000
ϕ_5	−16.97	b_1	0.0000	0.0000	0.0000	0.0000	0.0000	0.6284	0.0000	0.0000	0.0000	0.7779
ϕ_6	−14.52	b_2	0.4127	−0.4127	0.0000	0.3442	0.0000	0.0000	0.0000	−0.7354	0.0000	0.0000
ϕ_7	2.99	b_1	0.0000	0.0000	0.0000	0.0000	0.0000	0.7779	0.0000	0.0000	0.0000	−0.6284
ϕ_8	3.15	a_1	0.5154	0.5154	−0.6127	0.0000	0.1903	0.0000	0.0755	0.0000	−0.2267	0.0000
ϕ_9	6.34	b_2	0.4626	−0.4626	0.0000	−0.7361	0.0000	0.0000	0.0000	0.1746	0.0000	0.0000
ϕ_{10}	9.10	a_1	0.1449	0.1449	0.2169	0.0000	0.7063	0.0000	−0.3093	0.0000	0.5625	0.0000

*1 C-O axis taken as y axis; z axis perpendicular to molecular plane.

TABLE 2. CALCULATED LOWER EXCITED STATE OF FORMALDEHYDE

Exp.*1	Excited state	Energy (eV)	Symmetry	Nature of the excited state*2	Configurations mainly contributing to each state	
4.26	Φ_1	3.50	A_2	$n\rightarrow\pi^*$	$\Psi_{6\rightarrow7}$ (94.8%)	$\Psi_{3\rightarrow7}$ (5.2%)
	Φ_2	6.75	B_1	$\sigma\rightarrow\pi^*$	$\Psi_{4\rightarrow7}$ (98.4%)	
7.1	Φ_3	7.31	B_2	$n\rightarrow\sigma^*$	$\Psi_{6\rightarrow8}$ (61.4%)	$\Psi_{6\rightarrow10}$ (33.2%)
8.0	Φ_4	7.76	A_1	$\pi\rightarrow\pi^*$	$\Psi_{5\rightarrow7}$ (64.7%)	$\Psi_{4\rightarrow10}$ (17.7%)
	Φ_5	8.25	B_1	$\pi\rightarrow\sigma^*$	$\Psi_{5\rightarrow8}$ (81.5%)	$\Psi_{5\rightarrow10}$ (18.5%)

*1 Reference 7.

*2 A symbol "$n\rightarrow\pi^*$" is used when the excited state wave function is mainly consist of the configurations in which one electron in the ground configuration is excited from n(non-bonding)-orbital to π^*(π-anti-bonding)-orbital, and the transition from the ground state to this state is $n\rightarrow\pi^*$ transition.

absorptions are confirmed experimentally.[7] In the calculation of the H_2CO molecule, the C–H and C–O bond lengths were assumed to be 1.09 Å and 1.21 Å respectively,[8] and all the bond angles, to be 120°. We also assumed a planar structure with a C_{2v} symmetry for the ground and excited states. The SCF equations for closed-shell molecules derived by Pople *et al.* were used, and after the usual configurational interaction calculation for excited singlet states, the electronic transition energies for the H_2CO molecule were obtained. The values of β_H, β_C, and β_O were determined to be −8, −14, and −25 eV respectively. These values well reproduce the experimental $n\rightarrow\sigma^*$ and $\pi\rightarrow\pi^*$ transition energies, while for the $n\rightarrow\pi^*$ transition, the calculated energy was somewhat lower than the experimental one. The calculated SCF molecular orbitals are shown in Table 1, and the results of the configulation interaction treatment are shown in Table 2. By a number of calculations for the H_2CO molecule, the following results were also obtained: (1) the bonding parameter for the hydrogen atom does not change the calculated excitation energies so much as those of the carbon and oxygen atoms, (2) the parameters obtained, $\beta_H=-8$ eV, $\beta_C=-14$ eV, and $\beta_O=-25$ eV, almost completely reproduce the bond-order and electron-density matrix calculated by the parameters listed by Pople *et al.* but give a better agreement with the experimental transition energies than their parameters.

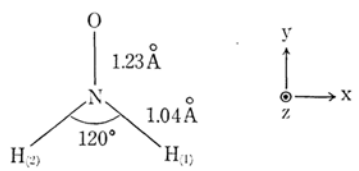

Fig. 1. Assumed structure of the H_2NO radical.[9]

The electronic structure of the H_2NO radical has been calculated assuming the planar configuration shown in Fig. 1. The bonding parameters obtained by calibration from the formaldehyde was used; for the bonding parameter of the nitrongen

7) H. Sponer and E. Teller, *Rev. Modern Phys.*, **13**, 75 (1941).

8) D. P. Stevensen, J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2508 (1939).

9) A. W. Hanson, *Acta Cryst.*, **6**, 32 (1953).

TABLE 3. LCAO SCF MO'S OF H_2NO RADICAL

MO	Orbital energy (eV)	Symmetry	Coefficients									
			1s(H_1)	1s(H_2)	2s(N)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)	2s(O)	$2p_x$(O)	$2p_y$(O)	$2p_z$(O)
ϕ_1	−41.24	a_1	0.1865	0.1865	0.5937	0.0000	0.2107	0.0000	0.7130	0.0000	−0.1590	0.0000
ϕ_2	−29.80	a_1	0.3180	0.3180	0.5577	0.0000	−0.3326	0.0000	−0.5781	0.0000	−0.2045	0.0000
ϕ_3	−22.90	b_2	0.3815	−0.3815	0.0000	0.6449	0.0000	0.0000	0.0000	0.5414	0.0000	0.0000
ϕ_4	−19.20	a_1	0.2194	0.2194	−0.0861	0.0000	−0.6240	0.0000	0.2867	0.0000	0.6518	0.0000
ϕ_5	−18.53	b_1	0.0000	0.0000	0.0000	0.0000	0.0000	0.7694	0.0000	0.0000	0.0000	0.6387
ϕ_6	−14.75	b_2	0.3335	−0.3335	0.0000	0.3012	0.0000	0.0000	0.0000	−0.8288	0.0000	0.0000
ϕ_7	−4.96	b_1	0.0000	0.0000	0.0000	0.0000	0.0000	0.6387	0.0000	0.0000	0.0000	−0.7694
ϕ_8	3.40	a_1	0.5403	0.5403	−0.5476	0.0000	0.1904	0.0000	0.0551	0.0000	−0.2779	0.0000
ϕ_9	6.99	b_2	0.4932	−0.4932	0.0000	−0.7024	0.0000	0.0000	0.0000	0.1471	0.0000	0.0000
ϕ_{10}	10.34	a_1	0.1552	0.1552	0.1713	0.0000	0.6476	0.0000	−0.2688	0.0000	0.6564	0.0000

TABLE 4. ELECTRON-DENSITY AND BOND-ORDER MATRIX OF H_2NO RADICAL

	1s(H_1)	1s(H_2)	2s(N)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)	2s(O)	$2p_x$(O)	$2p_y$(O)	$2p_z$(O)
1s(H_1)	0.8815	−0.1454	0.5384	0.6929	−0.4067	0.0000	0.0239	−0.1397	0.0966	0.0000
1s(H_2)		0.8815	0.5384	−0.6929	−0.4067	0.0000	0.0239	0.1397	0.0966	0.0000
2s(N)			1.3419	0.0000	−0.0134	0.0000	0.1524	0.0000	−0.5291	0.0000
$2p_x$(N)				1.0132	0.0000	0.0000	0.0000	0.1990	0.0000	0.0000
$2p_y$(N)					1.0886	0.0000	0.3272	0.0000	−0.7444	0.0000
$2p_z$(N)						1.5920	0.0000	0.0000	0.0000	0.4915
2s(O)							1.8494	0.0000	0.3835	0.0000
$2p_x$(O)								1.9599	0.0000	0.0000
$2p_y$(O)									0.9839	0.0000
$2p_z$(O)										1.4080

atom, β_N, the value of −20 eV was used for no particular reason. This value is between those for carbon and oxygen atoms; the effect of the variation in β_N on the results will be examined below. The orbital energies and LCAO coefficients obtained are listed in Table 3, and the bond-order and electron-density matrix, in Table 4. These tables show the following features of the electronic structure of the H_2NO radical:

(1) The ground-state electron configuration is:

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(2b_2)^2(2b_1)^1$$

where the orbitals, $3a_1$, $1b_1$, $2b_2$, and $2b_1$, are understood to be the N–O σ-bonding orbital (by the $2p_y$ atomic orbitals of the nitrogen and oxygen atoms), the π-bonding orbital (by the $2p_z$ orbitals of the nitrogen and oxygen atoms), the non-bonding orbital of the oxygen atom, and the π-anti-bonding orbital respectively. This electron configuration show that the odd electron occupies the anti-bonding π-orbital, that the non-bonding orbital ($2p_x$(O)) is the highest doubly-occupied orbital, and that this makes the nitric oxide radical have a large g_{yy} tensor in the ESR spectra.[10]

(2) The spin density on the oxygen atom is larger than that on the nitrogen atom. When only the π-system of the N–O group is considered, however, this difference is very small (Table 6).

(3) The coefficients for $2p_x$(O) show that the lone-pair orbital on the oxygen atom partially distributes on the hydrogen atoms through the pseudo-π-orbital constructed by two 1s orbitals of the hydrogen atoms and the $2p_x$ orbitals of the nitrogen and oxygen atoms.

In the configurational interaction treatment for the H_2NO radical, all singly-excited configurations of the form in Eq. (3) were considered. The energy levels and the configurations contributing to each state are tabulated in Table 5. The ground state has a B_1 symmetry, and the excited states are of 4 types, A_1, A_2, B_1, and B_2. The intensities are expected to be small for the transitions to A_1 and B_2 states because the basis set of the π-orbital is different from that of the non-bonding orbital or the σ-orbitals.*1 The $B_1 \rightarrow A_2$ ($n \rightarrow \sigma^*$) and the $B_1 \rightarrow B_1$ ($\pi \rightarrow \pi^*$) transitions will have strong intensities, but for the $n \rightarrow \sigma^*$ transitons it must be noted that the electronic oscillator strength is

10) O. H. Griffith, D. W. Cornell and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965).

*1 The predicted intensity of the $B_1 \rightarrow B_2$ transition will be zero for the electric-dipole radiation, and for the $B_1 \rightarrow A_1$ transition the transition moment will be finite as a result of the 2s atomic orbitals in the LCAO σ-orbital, but the intensity will not be strong.

TABLE 5. CALCULATED LOWER STATES OF H_2NO RADICAL

Exp.*1	State	Energy (eV)	Symmetry	Nature of the states*2	Configurations mainly contributing to each state			
	Φ_G	0.000	B_1	ground state	Ψ_g	(98.3%)		
2.76	Φ_{E1}	1.68	B_2	$n\rightarrow\pi^*$	$\Psi_{6\rightarrow7}$	(93.4%)	$\Psi_{3\rightarrow7}$	(6.6%)
	Φ_{E2}	2.96	A_1	$\pi\rightarrow\sigma^*$	$\Psi_{7\rightarrow8}$	(87.9%)	$\Psi_{5\rightarrow8}$(II)	(6.1%)
	Φ_{E3}	5.81	A_2	$n\rightarrow\sigma^*$	$\Psi_{6\rightarrow8}$(II)	(80.5%)	$\Psi_{6\rightarrow10}$(II)	(14.2%)
	Φ_{E4}	5.89	B_2	$\pi\rightarrow\sigma^*$	$\Psi_{7\rightarrow9}$	(85.3%)	$\Psi_{5\rightarrow9}$(II)	(11.0%)
5.17	Φ_{E5}	6.00	B_1	$\pi\rightarrow\pi^*$	$\Psi_{5\rightarrow7}$	(83.7%)	$\Psi_{4\rightarrow10}$(I)	(8.5%)
	Φ_{E6}	6.58	A_1	$\sigma\rightarrow\pi^*$	$\Psi_{4\rightarrow7}$	(97.9%)		
	Φ_{E7}	6.77	A_1	$\pi\rightarrow\sigma^*$	$\Psi_{5\rightarrow8}$(I)	(71.6%)	$\Psi_{5\rightarrow8}$(II)	(23.9%)
	Φ_{E8}	6.78	A_2	$n\rightarrow\sigma^*$	$\Psi_{6\rightarrow8}$(I)	(57.4%)	$\Psi_{6\rightarrow10}$(I)	(37.9%)

*1 Reference 2
*2 See the footnote of Table 2.

small for the $\Phi_G\rightarrow\Phi_{E3}$ transition because of the porperties of the two electronic wave functions, Φ_G and Φ_{E3}.*2 The calculated results indicate that the longest wavelength band corresponds to the $n\rightarrow\pi^*$ transition and that the two transitions at 6.00 eV and at 6.78 eV have strong intensities. As has been described before, Briere *et al.*[2] have reported the characteristic bands for aliphatic nitric oxide radicals, 2.76 eV (450 mμ, $\varepsilon=10$) and 5.17 eV (240 mμ, $\varepsilon=3000$). They assigned the band at 450 mμ to the $n\rightarrow\pi^*$ transition on the basis of its weak intensity and the facts that this band is sensitive to the polarity of the solvent and shifts to the shorter wavelength region in the polar solvent. The calculated energy for the $n\rightarrow\pi^*$ transition is lower than the experimental value by about 1 eV; this tendency also appeared in the calculation of the formaldehyde by the present calculation method. For the band at 240 mμ, from its intensity, they supposed it to be a $\pi\rightarrow\pi^*$ or $n\rightarrow\sigma^*$ transition. Their experimental results have also shown that this band is not sensitive to the polarity of the solvent and may be assigned to the $\pi\rightarrow\pi^*$ transition. The present calculated energy for the $\pi\rightarrow\pi^*$ is lower than that for the $n\rightarrow\sigma^*$ transition ($\Phi_G\rightarrow\Phi_{E8}$); this indicates that the band at 240 mμ corresponds to the $\pi\rightarrow\pi^*$ transition. A number of calculations for the H_2NO radical have shown that the above results for the H_2NO radical were consistent even with variations in the bonding parameter for the nitrogen atom (-15 —-23 eV) and in the N-O bond length (1.20—1.30 Å). Namely, the longest wavelength band has the $n\rightarrow\pi^*$ character, the transition energy for the $\pi\rightarrow\pi^*$ is always lower than that for $n\rightarrow\sigma^*$ ($\Phi_G\rightarrow\Phi_{E8}$ in Table 5), and some weak band exist in the ultraviolet and visible regions.

The $\pi\rightarrow\pi^*$ transition energy for the H_2NO radical, calculated by the method in which only the π-electrons were explicitly considered, is shown in Table 6. The calculation method and semi-empirical parameters used were the same as those reported elsewhere.[11] This result supports the assignment that the band at 240 mμ is the $\pi\rightarrow\pi^*$ transition.

TABLE 6. ENERGY LEVELS AND WAVE-FUNCTIONS OF H_2NO RADICAL*1

Energy (eV)	Wave-function*2
0.00	$\Phi_G = 0.999\lvert\phi_1\bar{\phi}_1\phi_2\rvert + 0.035\lvert\phi_1\bar{\phi}_2\phi_2\rvert$
5.77	$\Phi_E = 0.035\lvert\phi_1\bar{\phi}_1\phi_2\rvert - 0.999\lvert\phi_1\bar{\phi}_2\phi_2\rvert$

*1 π-electrons only were explicitly considered. The calculation method were same as that in Ref. 11.
*2 LCAO MO's are
$\phi_1 = 0.706$: $2p_z(N) + 0.708$: $2p_z(O)$
$\phi_2 = 0.708$: $2p_z(N) - 0.706$: $2p_z(O)$

The results for the $(CH_3)_2NO$ radical are added. The experimental values used in this paper are those for aliphatic nitric oxide radicals, and so the present calculations of the H_2NO radical do not strictly correspond to them. Therefore, the substituent effect on the results obtained above was examined. The results were parallel to those for the H_2NO radical; the calculated transition energies for the $(CH_3)_2NO$ radical corresponding to the $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$, and $n\rightarrow\sigma^*$ transitions of the H_2NO radical are 2.00, 6.77, and 8.33 eV respectively.

Some unsatisfactory points remain in this study: (1) In spite of the trial calculation for the H_2CO molecule, it is uncertain whether the method with CNDO approximation gives the proper results for the electronic transition energy of free radicals; (2) The molecular structure in the excited state was assumed to be the same as that of the ground state. In this study, the effect of these defects on the calculated results was not estimated and so some uncertainty may remain as to the assignment of

*2 $\langle\Psi_g\lvert\sum_n er_u\rvert\Psi_{i\rightarrow k}(\mathrm{II})\rangle = 0$ (See Table 5).

11) O. Kikuchi and K. Someno, This Bulletin, **40**, 2972 (1967).

the band at 240 mμ because the calculated $\pi \rightarrow \pi^*$ transition energy is near that of the $n \rightarrow \sigma^*$ transition.

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