The Ultraviolet Absorption Spectra of Nitramide and Ethyl Nitrate

By Koji KAYA, Keiji KUWATA and Saburo NAGAKURA

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The electronic absorption spectra of various molecules which contain both electron donating and accepting groups have been studied by several workers from both experimental and theoretical points of view.[1-9] Consequently, it has been found that these molecules exhibit absorption bands characteristic of the interaction between electron donor and acceptor. The absorption bands of this kind have been called intramolecular charge-transfer bands from an analogy with Mulliken's nomenclature[10] for the intermolecular case.

In the present paper, the study of the intramolecular charge-transfer band was extended to nitramide and ethyl nitrate, in which the nitro group as an electron acceptor and the amino or ethoxyl group as an electron donor are connected directly with each other. Our principal purposes are to discover intramolecular charge-transfer bands for these two systems, and to obtain quantitative knowledge about the interaction between the nitro group and the amino or ethoxyl group by combining the experimental data of the absorption spectra

1) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22** 236 (1954); S. Nagakura, ibid., **23** 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956).
2) J. Tanaka, This Bulletin, **36**, 833 (1963).
3) S. Nagakura, *Mol. Phys.*, **3**, 105 (1960); S. Nagakura, K. Kaya and H. Tsubomura, *J. Mol. Spectroscopy*, **13**, 1 (1964).
4) H. Hosoya, J. Tanaka and S. Nagakura, This Bulletin, 33, 850 (1960)
5) S. Nagakura, *Pure and Applied Chem.*, **7**, 79 (1963).
6) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).
7) J. N. Murrell, ibid., **A68**, 969 (1955).
8) J. N. Murrell, *Tetrahedron*, **19**, Suppl. 2, 277 (1963).
9) J. E. Bloor, *Canad. J. Chem.*, **39**, 2256 (1961)
10) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

with the theoretical results based on the molecular orbital calculations.

Experimental

Materials.—Ethyl nitrate was synthesized from ethanol and nitric acid.[11] It was purified by distillation and stored in a desiccator at low temperature.

Nitramide was synthesized by the decomposition of nitrourethane and was purified by recrystallization from petroleum ether.[12] It was stored in a desiccator with potassium hydroxide under reduced pressure and at low temperature.

Measurement.—The ultraviolet absorption measurements down to 1900 Å were made with a Cary recording spectrophotometer, model 14 M, quartz cells 0.1 and 1 cm. long being used.

A vacuum ultraviolet spectrophotometer constructed in our laboratory[13] was used for the measurements in the vacuum ultraviolet region. In this case, a quartz cell 0.01 cm. thick was used for the measurements of solutions, and gas cells 0.7 cm. and 3 cm. long and equipped with lithium fluoride windows were used for the measurements in the gaseous state.

The absorption spectra of nitramide and ethyl nitrate was measured in various solvents. We succeeded in measuring the absorption spectrum in the gaseous state for ethyl nitrate, but we could not do so for nitramide because of its explosive character at high temperatures. The observed absorption spectra are shown in Figs. 1 and 2. The peak wavelengths, molar extinction coefficients and oscillator strengths are tabulated in Table I.

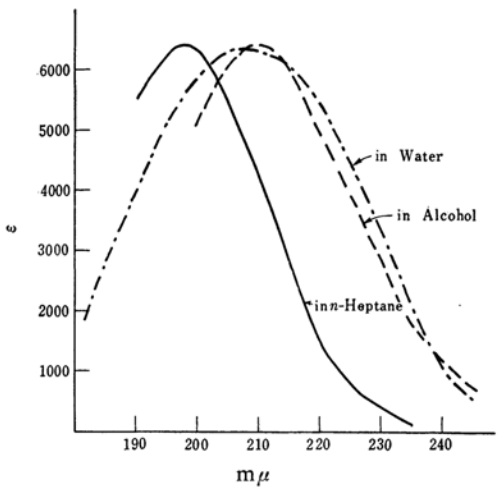

Fig. 1. The ultraviolet absorption spectra of nitramide.

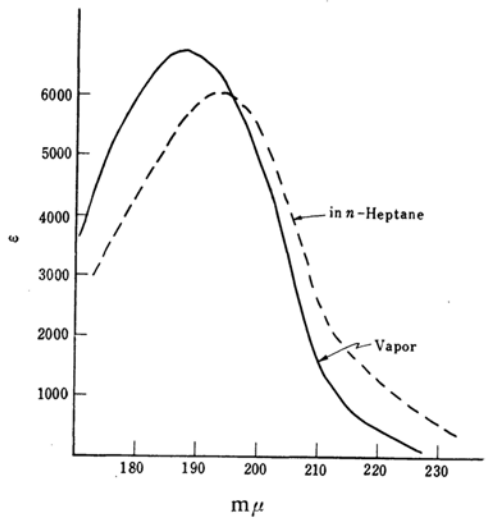

Fig. 2. The ultraviolet absorption spectra of ethyl nitrate.

TABLE I. THE OBSERVED PEAK WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS FOR NITRAMIDE AND ETHYL NITRATE

Sample	Solvent	λ_{max} (mμ)	ε_{max}
Nitramide	Water	207~208	6300
	Alcohol	209	6400
	n-Heptane	198	—
Ethyl nitrate	*n*-Heptane	193	5800
	Gas	190	6800

Theoretical

The π-electron energy levels and the wave functions of nitramide and ethyl nitrate were calculated by taking into account the configurational interaction among several electron configurations. That is to say, each of the two molecules was separated into the two components, the electron donor (NH_2 or C_2H_5O) and the electron acceptor (NO_2). The interaction between them was considered by means of the configurational interaction among π-electron configurations which have been constructed by putting the six π-electrons into the appropriate orbitals of the components. The electron configurations actually taken up in the present calculation are shown in Fig. 3. In addition to the ground configuration, G, a charge-transfer configuration, CT, which is caused by an electron transfer from the electron donor toward the electron acceptor, three locally excited configurations, LE_1, LE_2, LE_3, and one doubly excited configuration, D, were considered. A characteristic point in the present calculation is that we took the locally excited configuration LE_3, corresponding to the transition within the electron donating group,

11) L. Gattermann and H. Wieland, "Laboratory Method of Organic Chemistry," MacMillan and Co., Ltd., London (1952), p. 148.
12) C. A. Marlies, V. K. La Mer and J. Greenspan, "Inorg. Synth," Vol. 1, McGrow-Hill Book Co. Inc., New York (1939), p. 68.
13) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, 37, 818 (1964).

and the D configuration corresponding to a two electron excitation.

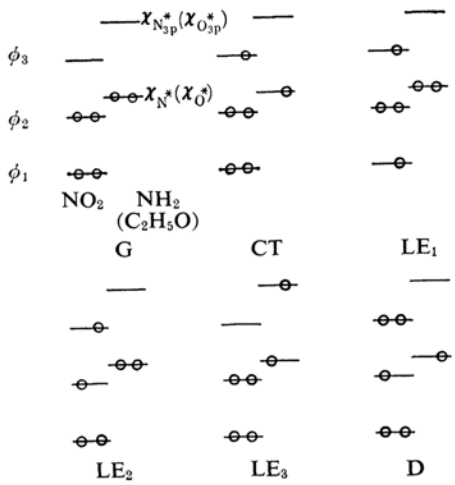

Fig. 3. The electron configurations of nitramide and ethyl nitrate.

The geometrical structure of nitramide was studied by Beevers and Trotman-Dickenson[14] with the X-ray crystal analysis technique and by Tyler[15] with the microwave spectrum analysis technique. The bond lengths and bond angles determined by the latter, which are shown in Fig. 4, were used in the present calculations. There has been no investigation of the structure of ethyl nitrate, so we assumed the structure of ethyl nitrate from the electron diffraction data of methyl nitrate by Pauling and Brockway[16] and from the X-ray crystal analysis data of pentaerythritol tetranitrate by Booth and Llewellyn.[17] The bond lengths and bond angles of ethyl nitrate used in the present calculation are also shown in Fig. 4.

The above-mentioned structure of ethyl

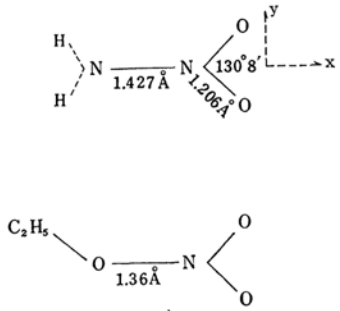

Fig. 4. The geometrical structures of nitramide and ethyl nitrate.

nitrate shows that the lone-pair electron orbital on the oxygen atom of the ethoxyl group is pure 2p. The situation is the same for planar nitramide. According to the study by Tyler, however, the two hydrogen atoms of the amino group of gaseous nitramide are out of the N–NO_2 plane by 51°47′. In this case, the lone-pair electron orbital of the nitrogen atom on the amino group can be represented by the hybridization of 2p and 2s orbitals.

In the present study, we first calculated the π-electron structures for the planar ethyl nitrate and nitramide molecules, and then we considered the effect of the distortion from the planarity for nitramide.

The energy of the ground configuration was taken as the standard. The energy of the charge-transfer configuration (H_{CT}) was calculated by the following equation:

$$H_{CT}=I_D-A_{NO_2}+E(D^+-A^-) \qquad (1)$$

Here, I_D is the ionization potential of the electron donating group (NH_2 or C_2H_5O); it was determined to be 10.25 and 10.44 eV. for the amino and ethoxyl groups respectively, from the ionization potentials of ammonia and ethanol obtained by Watanabe.[18] A_{NO_2} is the electron affinity of the electron accepting group (NO_2); it was assumed to be +0.40 eV, the value taken for a series of nitro compounds.[19,20] $E(D^+-A^-)$ is the electrostatic interaction energy between the electron donor and the acceptor after electron migration and can be represented by the following equations:

$$\left.\begin{aligned} &E(NH_2^+-NO_2^-)=0.4912(N^*N^* \mid NN)\\ &\quad -1.4912\ (N^*N^* \mid OO) \text{ for nitramide}\\ &E(C_2H_5O^+-NO_2^-)=0.4912(O^*O^* \mid NN)\\ &\quad -1.4912\ (O^*O^* \mid OO) \text{ for ethyl nitrate} \end{aligned}\right\} \qquad (2)$$

where $(\mu\mu \mid \nu\nu)$ indicates the two center Colomb repulsion integral between the $2p\pi$ atomic orbitals on the μ and ν atoms, and where N* is the nitrogen atom of the NH_2 group, O* is the oxygen atom of the C_2H_5O group, and N and O indicate the nitrogen and oxygen atoms of the NO_2 group respectively.

Two center Coulomb repulsion integrals were evaluated by Pariser and Parr's method.[21] The evaluation of these integrals needed valence state ionization potentials and electron affinities, so they were taken from the tables of Pritchard and Skinner[22] and of Moore[23].

14) C. A. Beevers and A. F. Trotman-Dickenson, *Acta Cryst.*, **10**, 34 (1957).
15) J. K. Tyler, *J. Mol. Spectr.*, **11**, 39 (1963).
16) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).
17) N. D. Booth and F. J. Llewellyn, *J. Chem. Soc.*, **1947**, 837.
18) K. Watanabe, *J. Chem. Phys.*, **22**, 1564 (1954).
19) S. Nagakura, *Mol. Phys.*, **3**, 152 (1960).
20) S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectroscopy*, in press.
21) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
22) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).
23) C. E. Moore, "Atomic Energy Levels" Vol. I, National Bureau of Standards (1949).

TABLE II. THE ENERGIES AND WAVE FUNCTIONS OF THE CONFIGURATIONS

Energy	Wave function[a]
$H_G=0$ eV.	$\varphi_G=(1\bar{1}2\bar{2}N^*\bar{N}^*)$
$H_{CT}=4.96$ eV. (NH_2NO_2) 5.13 eV. ($EtONO_2$)	$\varphi_{CT}=1/\sqrt{2}\{(1\bar{1}2\bar{2}N^*\bar{3})+(1\bar{1}2\bar{2}3\bar{N}^*)\}$
$H_{LE_1}=6.26$ eV.	$\varphi_{LE_1}=1/\sqrt{2}\{(1\bar{1}2\bar{3}\bar{N}^*N^*)+(1\bar{1}3\bar{2}N^*\bar{N}^*)\}$
$H_{LE_2}=11.15$ eV.	$\varphi_{LE_2}=1/\sqrt{2}\{(1\bar{3}2\bar{2}N^*\bar{N}^*)+(3\bar{1}2\bar{2}N^*\bar{N}^*)\}$
$H_{LE_3}=8.18$ eV. (NH_2NO_2) 10.99 eV. ($EtONO_2$)	$\varphi_{LE_3}=1/\sqrt{2}\{(1\bar{1}2\bar{2}N^*\bar{N}^*_{3p})+(1\bar{1}22N^*_{3p}N^*)\}$
$H_D=9.43$ eV.	$\varphi_D=1/\sqrt{2}\{(1\bar{1}233\bar{N}^*)+(1\bar{1}3\bar{2}N^*\bar{3})\}$

a) The exact formula for $(1\bar{1}2\bar{2}N^*\bar{N}^*)$ as an example is as follows;
$$(\bar{1}12\bar{2}N^*N^*)=1/\sqrt{6!}\sum(-1)^p p\begin{Bmatrix}\phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\chi_N^*(5)\phi_N^*(6)\\ \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\end{Bmatrix}$$ [b,c]

b) ϕ_1, ϕ_2 and ϕ_3 are the SCF molecular orbitals of the nitro group calculated by Tanaka *(J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78,** 1643(1957)) and are represented as below;
$\phi_1=0.7133\,\chi_N+0.7009/\sqrt{2}\,(\chi_O+\chi_{O'})$
$\phi_2=1/\sqrt{2}\,(\chi_O-\chi_{O'})$
$\phi_3=0.7009\,\chi_N-0.7133/\sqrt{2}\,(\chi_O+\chi_{O'})$
Here, χ_N and χ_O ($\chi_{O'}$,) indicate the $2p\pi$ atomic orbitals of the nitrogen and the two oxygen atoms of the nitro group.

c) χ_N^* and $\chi_N^*{}_{3p}$ are the $2p\pi$ and the $3p\pi$ atomic orbitals of the nitrogen atom of the amino group in the case of nitramide. In the case of ethyl nitrate, N^* and N^*_{3p} must be changed into χ_O^* and $\chi_O^*{}_{3p}$ which represent the $2p\pi$ and the $3p\pi$ atomic orbitals of the oxygen atom of the ethoxyl group.

TABLE III. THE OFF-DIAGONAL ELEMENTS USED IN THE PRESENT CALCULATION

$H_{G\cdot CT}=0.9912\ \beta_{NN}^*(\beta_{NO}^*)$ $\quad H_{CT\cdot LE_1}=-0.7133\ \beta_{NN}^*(\beta_{NO}^*)$
$H_{CT\cdot LE_3}=0.7009\ \beta_{NN}^*{}_{3p}\ (\beta_{NO}^*{}_{3p})$ $\quad H_{LE_2\cdot D}=0.7133\ \beta_{NN}^*(\beta_{NO}^*)$
$H_{G\cdot LE_1}=H_{G\cdot LE_3}=H_{CT\cdot LE_2}=H_{LE_1\cdot LE_3}=0$

$\beta_{NN}^*=\int\chi_N H_{core}\chi_N^*d\tau=-2.14$ eV. $\quad \beta_{NO}^*=\int\chi_N H_{core}\chi_O^*d\tau=-2.18$ eV.

$\beta_{NN}^*{}_{3p}=\int\chi_N H_{core}\chi_N^*{}_{3p}d\tau=-2.52$ eV. $\quad \beta_{NO}^*{}_{3p}=\int\chi_N H_{core}\chi_O^*{}_{3p}d\tau=-2.49$ eV.

As has been mentioned above, we considered three locally excited configurations, LE_1, LE_2, LE_3. Among these, LE_1 and LE_2 are caused by local excitation within the nitro group. The energy of the LE_2 configuration, H_{LE2}, is lower than that of the LE_1 configuration. H_{LE2} was taken to be 6.26 eV. from the position of the observed $\pi\rightarrow\pi^*$ transition band of nitromethane.[19] Concerning the energy of the locally excited configuration LE_1, the corresponding value has never been observed; therefore, it was calculated by the following equation:

$$H_{LE1}=-2\sqrt{2}\,\beta_{NO}+K_{13} \qquad (3)$$

where β_{NO} is the core resonance integral between the $2p\pi$ atomic orbitals of the nitrogen and oxygen atoms of the nitro group and K_{13} represents the exchange repulsion integral between the lowest (ϕ_1) and the highest (ϕ_3) π molecular orbitals of the nitro group, the actual forms of which are shown in Table II. The value of β_{NO} was calculated by the following approximate equation: [24]

$$\beta_{\mu\nu}=\frac{(I_\mu+I_\nu)S_{\mu\nu}\beta_{CC}}{2(I_C S_{CC})} \qquad (4)$$

Here, I_μ I_ν and I_C are the ionization potentials of the μ atom, the ν atom and the carbon atom of benzene respectively. $S_{\mu\nu}$ and S_{C-C} are the overlap integrals between $2p\pi$ atomic orbitals of the μ and ν atoms[25] and between the $2p\pi$ atomic orbitals of the neighboring carbon atoms of benzene respectively. By the use of the above equation, β_{NO} was evaluated to be -3.25 eV. The K_{13} value was resolved into two center Coulomb integrals and found to be 1.96 eV. Therefore, the value of H_{LE} was determined to be 11.15 eV.

The energy of the LE_3 configuration corresponding to the $2p\rightarrow3p$ transition within the

24) R. S. Mulliken, *J. Phys. Chem.*, **56,** 295 (1952).
25) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff *J. Chem. Phys.*, **17,** 210 (1949).

TABLE IV. THE WAVE FUNCTIONS FINALLY OBTAINED WITH NITRAMIDE AND ETHYL NITRATE

Nitramide (planar)

Energy, eV.	Wave function
$W_0=-0.85$	$\phi_0=0.9244\,\varphi_G+0.3714\,\varphi_{CT}-0.0472\,\varphi_{LE_1}+0.0725\,\varphi_{LE_3}$
$W_1=4.67$	$\phi_1=-0.3684\,\varphi_G+0.8128\,\varphi_{CT}-0.1912\,\varphi_{LE_1}+0.4088\varphi_{LE_3}$
$W_2=5.65$	$\phi_2=0.9280\,\varphi_{LE2}+0.3726\,\varphi_D$
$W_3=8.88$	$\phi_3=0.0851\,\varphi_G-0.3571\,\varphi_{CT}+0.2398\,\varphi_{LE_1}+0.8988\,\varphi_{LE_3}$
$W_4=10.04$	$\phi_4=-0.3726\,\varphi_{LE_2}+0.9280\,\varphi_D$
$W_5=11.59$	$\phi_5=-0.0497\,\varphi_G+0.2720\,\varphi_{CT}+0.9506\,\varphi_{LE_1}-0.1409\,\varphi_{LE_3}$

Nitramide (non-planar)

Energy, eV.	Wave function
$W_0=-0.63$	$\phi_0=0.9433\,\varphi_G+0.3250\,\varphi_{CT}-0.0364\,\varphi_{LE_1}+0.0564\,\varphi_{LE_3}$
$W_1=4.83$	$\phi_1=-0.3125\,\varphi_G+0.8462\,\varphi_{CT}-0.1769\,\varphi_{LE_1}+0.3864\,\varphi_{LE_3}$
$W_2=5.80$	$\phi_2=0.9546\,\varphi_{LE_2}+0.2979\,\varphi_D$
$W_3=8.76$	$\phi_3=0.0732\,\varphi_G-0.3492\,\varphi_{CT}+0.1933\,\varphi_{LE_1}+0.9140\,\varphi_{LE_3}$
$W_4=9.96$	$\phi_4=-0.2979\,\varphi_{LE_2}+0.9546\,\varphi_D$
$W_5=11.48$	$\phi_5=-0.0380\,\varphi_G+0.2375\,\varphi_{CT}+0.9644\,\varphi_{LE_1}-0.1102\,\varphi_{LE_3}$

Ethyl nitrate

Energy, eV.	Wave function
$W_0=-0.85$	$\phi_0=0.9287\,\varphi_G+0.3639\,\varphi_{CT}-0.0472\,\varphi_{LE_1}+0.0537\,\varphi_{LE_3}$
$W_1=5.12$	$\phi_1=-0.3656\,\varphi_G+0.8661\,\varphi_{CT}-0.2233\,\varphi_{LE_1}+0.2576\,\varphi_{LE_3}$
$W_2=5.64$	$\phi_2=0.9273\,\varphi_{LE_2}+0.3744\,\varphi_D$
$W_3=10.04$	$\phi_3=-0.3744\,\varphi_{LE_2}+0.9273\,\varphi_D$
$W_4=11.07$	$\phi_4=0.0067\,\varphi_G-0.0343\,\varphi_{CT}+0.6900\,\varphi_{LE_1}+0.7229\,\varphi_{LE_3}$
$W_5=11.92$	$\phi_5=-0.0618\,\varphi_G+0.3410\,\varphi_{CT}+0.6869\,\varphi_{LE_1}-0.6388\,\varphi_{LE_3}$

TABLE V. THE OBSERVED AND CALCULATED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

	Transition	Transition energy, eV.			Oscillator strength	
			Obs.	Cald.	Obs.	Cald.
Nitramide	W_0-W_1	5.94	6.26	5.52	0.233	0.11
	W_0-W_2			6.50		0.61
Ethyl nitrate	W_0-W_1	6.43	6.52	5.97	0.233	0.15
	W_0-W_2			6.49		0.59

electron-donating group was determined to be 8.18 eV. and 10.99 eV. for the NH_2 and C_2H_5O groups, respectively. The former value was obtained by adding the energy difference between the 3s and 3p orbitals[23] to the observed Rydberg transition energy of ammonia.[26] The latter value was assumed to be equal to the difference between the 2p and 3p orbitals of the oxygen atom taken form Moore's table.[23] The energy of the doubly excited configuration D was evaluated by the following equation:

$$H_D=H_{LE_1}+I_D-A_{NO_2}{}^*+E^*(D^+-A^-)$$
$$=9.430\text{ eV. for } NH_2NO_2$$
$$=9.426\text{ eV. for } EtONO_2 \qquad (5)$$

Here $A_{NO_2}{}^*$ is the electron affinity for bringing an additional electron into the ϕ_3 orbital of the nitro group in the locally excited state LE_2; it was assumed to be 1.03 eV.[27] $E^*(D^+-A^-)$ is the electrostatic interaction energy between the electon donating and accepting groups in the D configuration and was evaluated by the use of the above-mentioned two center Coulomb integrals of the $(\mu\mu\,|\,\nu\nu)$ type. The energies and the wave functions of the configurations used in the present calculations are tabulated in Table II.

The off-diagonal matrix elements of the total electronic Hamiltonian which represent the magnitudes of the interaction between different configurations were evaluated according to the formulations by Pople[28] and by Longuet-Higgins and Murrell.[6] They are given in Table III in terms of the core resonance integrals $\beta_{NO}{}^*$, $\beta_{NN}{}^*$, $\beta_{NO_3p}{}^*$ and $\beta_{NN3p}{}^*$. The definitions and values of these

26) A. B. F. Duncan, *Phys. Rev.*, **50**, 700 (1936).

27) According to the exact calculations, the energy difference between A^*_{NO2} and A_{NO2} can be written as follows:

$$A^*_{NO2}-A_{NO2}=J_{23}+K_{23}-J_{33}=+0.63\text{ eV.} \qquad (6)$$

Here, J_{ij} and K_{ij} represent, respectively, the Coulomb and exchange repulsion integrals between the ϕ_i and ϕ_j molecular orbitals of the nitro group.

28) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

core resonance integrals evaluated by Eq. 4 are also shown in Table III.

Using these diagonal and off-diagonal matrix elements, we set up the secular equations of the fourth and second orders for the symmetric and antisymmetric configurations respectively. Solving these equations by an electronic computer, a Facom 202 in our Institute, we obtained the π-electron energy levels and the wave functions for planar nitramide and ethyl nitrate. The energy levels and wave functions are shown in Figs. 5 and 6 and in Table IV. From these results, the transition

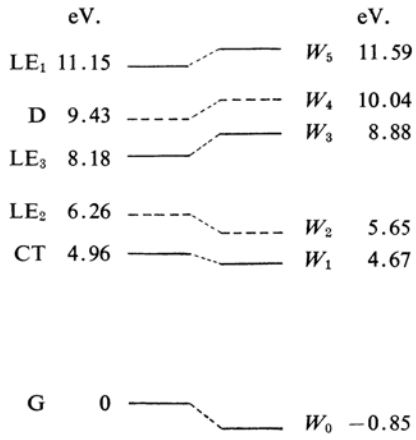

Fig. 5. The π-electron energy levels of nitramide.

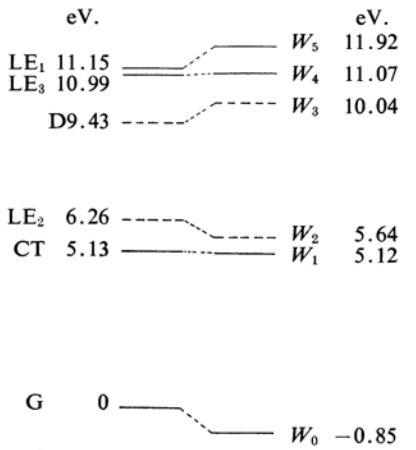

Fig. 6. The π-electron energy levels of ethyl nitrate.

energies and oscillator strengths were calculated for the longest two $\pi \rightarrow \pi^*$ transition bands of nitramide and of ethyl nitrate. The results are shown in Table V, together with the observed results.

As may be seen in the paper by Tyler,[15] there is some doubt concerning the planar structure of nitramide. Therefore, it seems to be necessary to consider the effect of the distortion from planarity on the absorption spectrum of nitramide.

From one 2s and three 2p atomic orbitals of the nitrogen atom of the amino group, four hybridized orbitals, which are independent and orthonormal from each other, are constructed; two of them are directed towards the two hydrogen atoms of the amino group, and the third one, towards the nitrogen atom of the nitro group. The last one constitutes the lone pair electron orbital of the amino group. If we take the coordinate of the molecule as shown in Fig. 4, the geometrical structure of nitramide determined by Tyler leads to the conclusion that the principal axis of the lone pair orbital is on the xz plane and makes an angle of 14°35′ from the z axis.

Since this angle is rather small and therefore, the lone pair electron orbital has an overwhelmingly large contribution from the π-electron orbital,[29] the effect of distortion from the planarity of the molecule on the calculated energy levels and wave functions may be thought to be small. This is shown to be true by the actual calculations. The theoretical result calculated by considering the changes of the core resonance integral β_{NN}^* and of the two center Coulomb integrals due to the distortion from the planarity is very similar to that for the planar molecule, as is seen in Table IV. Therefore, we will hereafter consider only the case of planar nitramide.

Results and Discussion

As is easily seen in Figs. 1 and 2, both nitramide and ethyl nitrate show rather broad bands near 200 mμ. The peak wave lengths and the molar extinction coefficients obtained by us are summarized in Table I. The ultraviolet spectrum of nitramide was first measured by Jones.[30] According to his results, nitramide has its absorption maximum at 225 mμ in an aqueous solution. This result is obviously different from our result, which shows the absorption maximum near 200 mμ. Our sample was identified by the aid of the infrared absorption measurements and of the elementary analysis of nitrogen. Therefore, Jones' finding on the ultraviolet absorption spectrum of nitramide may conceivably be erroneous.

According to the theoretical results shown

29) The lone pair orbital of the amino group ϕ_N^* can be written as follows:
$$\phi_N^* = 0.4448\ \chi_{2s} + 0.8668\ \chi_{2pz} + 0.2255\ \chi_{2px}$$
where χ_{2s}, χ_{2qz} and χ_{2px} represent the 2s, $2p_z$ and $2p_x$ atomic orbital wave functions on the nitrogen atom of the amino group.

30) R. Jones, *Canad. J. Reaserch*, **B27**, 828 (1949).

in Table V, the first $\pi \rightarrow \pi^*$ band corresponding to the $W_0 \rightarrow W_1$ transition should appear at 225 and 208 mμ for nitramide and ethyl nitrate respectively, with the oscillator strength value of 0.14 and 0.15. As will be mentioned below, however, another strong band corresponding to the $W_0 \rightarrow W_2$ transition may be expected to appear near 200 mμ for either of these two molecules. Therefore, it seems reasonable to consider that the $W_0 \rightarrow W_1$ transition band may be covered by the $W_0 \rightarrow W_2$ transition band. This expectation seems to be supported by the broadness of the observed bands. As may easily be seen by comparing the wave function of the first excited state with that of the ground state, the first $\pi \rightarrow \pi^*$ band may be regarded as an intramolecular charge-transfer band caused by interaction between the electron donating group (NH_2 or OC_2H_5) and the electron accepting group (NO_2).

The present calculation shows that near 200 mμ there should exist the $W_0 \rightarrow W_2$ transition bands, which have the character of local excitation within the nitro group. Their calculated oscillator strengths are 0.61 and 0.59 for nitramide and ethyl nitrate respectively. Therefore, the observed broad bands of nitramide and ethyl nitrate can be interpreted as the superposition of the two bands corresponding to the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions. Of course, the $W_0 \rightarrow W_2$ transition band makes the main contribution to the observed band, since the calculated oscillator strength value of this band is about five times larger than that of the $W_0 \rightarrow W_1$ transition band.

By looking at the findings on the energy value, W_0, of the ground state given in Table IV, it may be seen that the ground state is lower by 0.85 eV. = 19.5 kcal./mol. for both nitramide and ethyl nitrate than the unperturbed ground configuration. These stabilization energies, which are mainly brought about by interaction between the ground and charge-transfer configurations, may be regarded as corresponding to the vertical resonance energy due to the resonance hybrid between the following two structures for each molecule:

$$H_2N\text{–}NO_2 \leftrightarrow H_2N^+\text{=}NO_2^-$$

$$H_5C_2O\text{–}NO_2 \leftrightarrow H_5C_2O^+\text{=}NO_2^-$$

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo (K. Kaya and S. N.)

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka (K. Kuwata)