Lower Electronic States of the Free NH_2 *Radical*[1]

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Introduction

Free radicals like CH_2, CH_3, NH_2 and others have been assumed to be intermediates in many chemical reactions, but their existence has not definitely been identified. Recently, the flash technique was applied to the spectroscopy by Porter[2], and the existence of some free radicals has been identified. For such polyatomic free radicals, however, only limited information should be expected about the electronic states and the structures, because at present many levels have not yet been identified experimentally even for stable molecules. Thus, it is very difficult to determine the course of such reactions as photolysis or electric discharge, in which the role of electronic excited states is of great significance. The theoretical interpretation is, therefore, very important not only as a supplement to observation but as the discussion of chemical reaction, in which such a radical is assumed to exist as an intermediate.

The so-called α band of ammonia has long been known from emission spectra of oxy-ammonia flames and electric discharges through ammonia,[3] and has long been suspected of being due to the free NH_2 radical. Recently, Herzberg and Ramsay[4] observed the α bands in absorption in photodecomposed ammonia by using a flash technique and confirmed the fact that the free NH_2 radical is responsible for the α band. Little, has, however, been done on the theoretical interpretation.

Thus, the lower electronic states and the structure of the free NH_2 radical are theoretically investigated in the present work. The method used is the LCAO-SCF one developed by Roothaan[5] and the SCF calculation is performed for the ground state only. The energy levels of the lower excited states are computed by use of the ground state MO's without configuration interaction, because some reasonable results have been obtained on the CH radical in a similar way[6] and such reliable results may also be expected here if reasonable values of energy integrals can be used.

Outline of Calculation

The calculation was performed by assuming the spatial configuration of the NH_2 radical as an isosceles triangle, and taking the x and y axes in the molecular plane and the z axis being perpendicular to the plane as shown in Fig. 1. The internuclear distance between the nitrogen and the hydrogen was

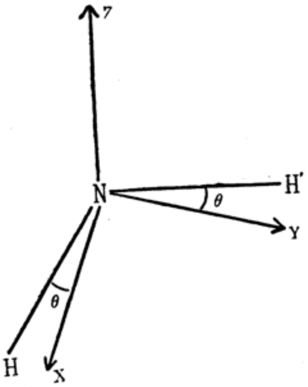

Fig. 1. Axes for the NH_2 radical.

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[1] A preliminary account of the present paper was given in *J. Chem. Phys.*, **22**, 1467 (1954).

[2] G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950).

[3] W. B. Rimmer, *Proc. Roy. Soc.* (*London*), **A103**, 696 (1923); F. Fowler and J.S. Badami, *Proc. Roy. Soc.* (*London*), **A133**, 325 (1931); A. G. Gaydon, *Proc. Roy. Soc.* (*London*), **A181**, 197 (1942).

[4] G. Herzberg and D.A. Ramsay, *J. Chem. Phys.*, **20**, 347 (1952); *Discussion Faraday Soc.*, No. 14, 11 (1952).

[5] C.C.J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[6] J. Higuchi, *J. Chem. Phys.*, **22**, 1339 (1954).

taken as 1.01 Å as in the equilibrium distance of the ammonia molecule7).

NH_2 is a nine-electron radical, and the LCAO-SCF calculation was carried out by taking the seven atomic orbitals n, s, x, y, z, h and h' into consideration, which mean 1s, 2s, 2px, 2py, 2pz orbitals of nitrogen atom, 1s of one hydrogen (the side of the x axis) and 1s of the other hydrogen, respectively. The interactions between all electrons were explicitly included but the orthogonality between n and h or h' was assumed, because its overlap integral is fairly small in comparison with the others8).

The atomic orbitals used were the Hartree-Fock SCF AO's in the ^4S state of nitrogen9) and in the ^2S state of hydrogen. The majority of the two-center integrals is, however, very difficult to calculate, and it was, therefore, assumed that the use of Slater AO's10) instead of the SCF AO's gives satisfactory approximations of the two-center integrals, and they were taken from the table by Kotani and Amemiya.11) The core-field energies were, however, obtained from the Fock equations of the ^4S state of nitrogen atom as in the case of the CH radical6). The one-electron three-center integrals for the nitrogen-hydrogen type were calculated by following Oohata's method12), but for the hydrogen-hydrogen type were taken from the table by Hirschfelder and Weygandt13), while the two-electron integrals were approximately obtained by modifying Mulliken's approximation14).

LACO MO's ϕ's which are formed by these seven atomic orbitals χ_p's were chosen so that they belong in sets to irreducible representations of the symmetry C_{2v} of NH_2, and they are reduced to15)

$$
\begin{aligned}
K(a_1)&=n\\
1a_1&=a_{11}(s)+a_{12}(x+y)+a_{13}(h+h')\\
2a_1&=a_{21}(s)+a_{22}(x+y)+a_{23}(h+h')\\
3a_1&=a_{31}(s)+a_{32}(x+y)+a_{33}(h+h') \qquad (1)\\
1b_1&=z\\
1b_2&=a_{44}(x-y)+a_{45}(h-h')\\
2b_2&=a_{54}(x-y)+a_{55}(h-h')
\end{aligned}
$$

Here the order of increasing number for the MO's within each symmetry species is the order of increasing energy. The coefficients a_{ip}'s of atomic orbitals χ_p's were chosen to satisfy the orthonormality conditions:

$$\int\bar{\phi}_i^{\nu}\phi_j^{\nu}d\tau^{\nu}=\sum_{p,q}\bar{a}_{ip}S_{pq}a_{jq}=\delta_{ij}, \qquad (2)$$

where the overlap integrals S_{pq}'s are defined by

$$S_{pq}=\bar{S}_{qp}=\int\bar{\chi}_p\chi_q d\tau. \qquad (3)$$

The electronic structure of the $^2B_1$ state, which has been considered to be the ground state of the NH_2 radical, is given as resulting from configuration $(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^1$, and the total nine electron normalized wave function Φ for this state is then built up as an antisymmetrized product of these LCAO MO's and the energy of this state is given by

$$E=\int\bar{\Phi}\mathfrak{H}\Phi d\tau. \qquad (4)$$

where

$$\mathfrak{H}=\sum_{\mu=1}^{9}\left(-\frac{1}{2}\Delta_{\nu}-\frac{7}{r_{N\nu}}-\frac{1}{r_{H\nu}}-\frac{1}{r_{H'\nu}}\right)+\frac{1}{2}\sum_{\substack{\mu,\nu=1\\ \mu\neq\nu}}^{9}\frac{1}{r^{\mu\nu}} \qquad (5)$$

Introducing the notations

$$H_i=\int\bar{\phi}_i^{\nu}\left(-\frac{1}{2}\Delta_{\nu}-\frac{7}{r_{N\nu}}-\frac{1}{r_{H\nu}}-\frac{1}{r_{H'\nu}}\right)\psi_i^{\nu}d\tau^{\nu} \qquad (6)$$

$$J_{ij}=\int\bar{\phi}_i^{\mu}\bar{\phi}_j^{\nu}\frac{1}{r^{\mu\nu}}\phi_i^{\mu}\phi_j^{\nu}d\tau^{\mu\nu} \qquad (7)$$

$$K_{ij}=\int\bar{\phi}_i^{\mu}\bar{\phi}_j^{\nu}\frac{1}{r^{\mu\nu}}\varphi_j^{\mu}\phi_i^{\nu}d\tau^{\mu\nu} \qquad (8)$$

and

$$H'_i=H_i+2J_{ni}-K_{ni}, \qquad (6')$$

one obtains

$$
\begin{aligned}
E=&2H_n+J_{nn}+2H'_{1a_1}+2H'_{1b_2}+2H'_{2a_1}\\
&+H'_{1b_1}+J_{1a_11a_1}+4J_{1a_11b_2}-2K_{1a_11b_2}\\
&+4J_{1a_12a_1}-2K_{1a_12a_1}+2J_{1a_11b_1}-K_{1a_11b_1}\\
&+J_{1b_21b_2}+4J_{1b_22a_1}-2K_{1b_22a_1}+2J_{1b_21b_1}\\
&-K_{1b_21b_1}+J_{2a_12a_1}+2J_{2a_11b_1}-K_{2a_11b_1}. \qquad (9)
\end{aligned}
$$

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7) H. Sponer, "Molekülspektren I. Tabellen", Verlag Julius Springer Berlin, (1935) p. 80.

8) $S_{nh}=0.0678$, while $S_{sh}=0.5601$ and $S_{\sigma h}=0.4187$.

9) D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* (*London*), **A193**, 299 (1948).

10) $n=(\delta'^3/\pi)^{1/2}\exp(-\delta' r)$, $s=(\delta^5/3\pi)^{1/2}r\exp(-\delta r)$, $\sigma=(\delta^5/\pi)^{1/2}r\exp(-\delta r)\cos\theta$, $\pi=(\delta^5/\pi)^{1/2}r\exp(-\delta r)\sin\theta\begin{Bmatrix}\cos\phi\\ \sin\phi\end{Bmatrix}$ and $h=(1/\pi)^{1/2}\exp(-r)$. In the present paper, δ and δ' are chosen as 1.90 and 6.757, respectively.

11) M. Kotani and A. Amemiya, *Proc. Phys. Math. Soc. Japan*, **22**, Extra No. 1 (1940).

12) K. Oohata, *Busseiron Kenkyu*, **50**, 38 (1952).

13) J.O. Hirschfelder and C.N. Weygandt, *J. Chem. Phys.*, **6**, 806 (1938).

14) R. S. Mulliken, *J. chim. phys.*, **46**, 500 and 521 (1949).

Some values calculated by Mulliken's approximation are rather small as compared with the exact values, for example in the case of the one-electron integrals for the hydrogen-hydrogen type. In the present work, therefore, the two-electron three-center integrals were obtained from the exact value of one-electron three-center integrals as follows:

$$(\alpha\beta:\gamma\delta)=(1/4)T_{\alpha\beta}T_{\gamma\delta}[(\alpha\alpha:\gamma\gamma)+(\beta\beta:\gamma\gamma)+(\alpha\alpha:\delta\delta)+(\beta\beta:\delta\delta)]$$

where

$$T_{\alpha\beta}=2(P_{\gamma\delta}:\alpha\beta)/[(P_{\gamma\delta}:\alpha\alpha)+(P_{\gamma\delta}:\beta\beta)].$$

Here the $P_{\gamma\delta}$ is the point which was found by maximizing the overlapping charge $\chi_\gamma\chi_\delta d\tau$ along the internuclear axis. This approximation gives fairly good results in two-center integrals but somewhat doubtful results from the point of view of physical meaning. It is, therefore, more desirable to use the higher order expansion of atomic orbitals.

15) In the present work, the choice of the symmetry axis is made according to Mulliken.

To obtain the $1a_1$, $1b_2$ and $2a_1$ orbitals, a variational procedure was carried out for the energy of state (4), subject to the orthonormality conditions of the MO's (1). It can be shown that this variational process leads to the following equation

$$(\boldsymbol{H}'+\boldsymbol{G})\boldsymbol{a}_i=\epsilon_{ii}\boldsymbol{S}\boldsymbol{a}_i. \tag{10}$$

Here the column vectors $\boldsymbol{a}_i$'s give the coefficients of the AO's in the ia_1 and ib_2 orbitals. $\boldsymbol{S}$ is a hermitian matrix with elements given by (3); $\boldsymbol{H}'$ is the core-field energy matrix with elements

$$H'_{pq}=\overline{H}'_{qp}=\int\overline{\chi}_p{}^v\left(-\frac{1}{2}\Delta_v-\frac{7}{r_{Nv}}-\frac{1}{r_{Hv}}-\frac{1}{r_{H'v}}\right)\chi_q{}^v d\tau^v+2(pq:nn)-(pn:nq), \tag{11}$$

where

$$(pq:rt)=\int\overline{\varphi}_p{}^\mu\overline{\varphi}_r{}^v\frac{1}{r_{\mu v}}\varphi_q{}^\mu\varphi_t{}^v d\tau^{\mu v}.^{16)} \tag{12}$$

$\boldsymbol{G}$ is the electronic interaction matrix with elements

$$\begin{aligned}G_{pq}=\overline{G}_{qp}=&2(pq:1a_11a_1)-(p1a_1:1a_1q)\\&+2(pq:1b_21b_2)-(p1b_2:1b_2q)\\&+2(pq:2a_12a_1)-(p2a_1:2a_1q)\\&+(pq:1b_11b_1)-(1/2)(p1b_1:1b_1q).\end{aligned} \tag{13}$$

The procedure followed in the calculation is to assume values of $\boldsymbol{a}_i$'s in (1) consistent with the orthonormality conditions (2), compute the G_{pq}'s by (13), solve Eq. (10) for ϵ_{ii} and a new set $\boldsymbol{a}_i$'s and repeat until self-consistency is attained.

LCAO MO's

The LCAO MO's of the lowest energy of the $^2B_1$ state by the SCF procedure are given in Table I, and the orbital energies are plotted in Fig. 2. These LCAO MO's are considered to be reasonable for that state, and their electronic properties can be regarded as corresponding to those of H_2O by Ellison and Shull[17] and by Maeda[18], which are also calculated by the LCAO-SCF method, because the NH_2 and H_2O are molecules belonging to the same symmetry group C_{2v}. That is, the $1a_1$ orbital indicates strong bonding property, for the coefficient of s is much larger than the others, but $2a_1$ orbital is weakly bonding due to strong s-p mixing in the nitrogen orbitals of the MO at the bond angle near the equilibrium point. Such natures of the σ orbitals discussed in the case of the CH radical[6] are considered to be quite similar to those of the a_1 orbitals in

TABLE I

LCAO-SCF MO'S FOR THE $^2B_1$ STATE

$K(a_1)=n$

$$1a_1=\begin{pmatrix}0.762\\0.759\\0.753\\0.742\\0.737\end{pmatrix}(s)+\begin{pmatrix}0.151\\0.132\\0.112\\0.067\\0.000\end{pmatrix}(x+y)+\begin{pmatrix}0.156\\0.166\\0.179\\0.200\\0.211\end{pmatrix}(h+h')$$

$$2a_1=-\begin{pmatrix}0.618\\0.578\\0.531\\0.355\\0.000\end{pmatrix}(s)+\begin{pmatrix}0.533\\0.561\\0.590\\0.661\\0.707\end{pmatrix}(x+y)+\begin{pmatrix}0.245\\0.237\\0.227\\0.159\\0.000\end{pmatrix}(h+h')$$

$$3a_1=\begin{pmatrix}1.031\\1.075\\1.111\\1.183\\1.235\end{pmatrix}(s)+\begin{pmatrix}0.580\\0.527\\0.464\\0.281\\0.000\end{pmatrix}(x+y)-\begin{pmatrix}0.856\\0.875\\0.883\\0.891\\0.898\end{pmatrix}(h+h')$$

$1b_1=z$

$$1b_2=\begin{pmatrix}0.397\\0.389\\0.386\\0.385\\0.392\end{pmatrix}(x-y)+\begin{pmatrix}0.532\\0.503\\0.479\\0.449\\0.431\end{pmatrix}(h-h')$$

$$2b_2=\begin{pmatrix}0.746\\0.777\\0.805\\0.851\\0.866\end{pmatrix}(x-y)+\begin{pmatrix}0.968\\0.949\\0.948\\0.967\\0.983\end{pmatrix}(h-h')$$

at the bond angle of $\begin{pmatrix}90°\\115°\\120°\\150°\\180°\end{pmatrix}$, respectively.

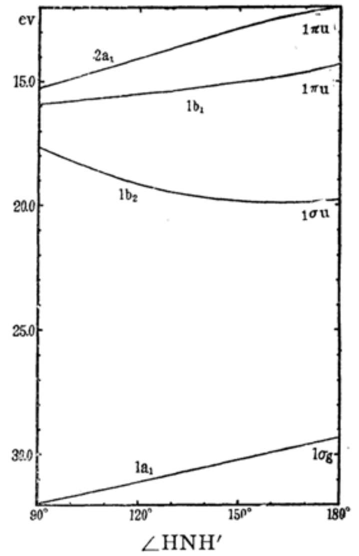

Fig. 2. Ionization energies for the $^2B_1$ state of the NH_2 radical. The value for the linear form are given as the extrapolated one from the non-linear form.

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[16] Orbitals φ_p's mean either AO's χ_p's or MO's ϕ_p's.

[17] F. O. Ellison and H. Shull, *J. Chem. Phys.*, 21, 1420 (1953).

[18] S. Maeda, *Busseiron Kenkyu*, 70, 101 (1954).

this case. That is, the a_1 (or σ) orbital of the lowest energy except the inner shell is strongly bonding but the a_1 (or σ) orbitals of higher energies are weakly bonding.

It is seen that the coefficients of $x-y$ in the $1b_2$ orbitals are almost independent of the bond angle, while others are not. On the other hand, the hybridized orbitals used in the electron pair bond theory[19] are written as follows:

$$\begin{aligned} \Psi_1 &= (1/2)^{1/2}(s)\cos\alpha-(1/2)(x+y)\sin\alpha \\ &\quad +(1/2)(x-y) \\ \psi_2 &= (1/2)^{1/2}(s)\cos\alpha-(1/2)(x+y)\sin\alpha \\ &\quad -(1/2)(x-y) \qquad (14) \\ \psi_3 &= (s)\sin\alpha+(1/2)^{1/2}(x+y)\cos\alpha \end{aligned}$$

where

$$\sin\alpha=(1-\tan\theta')/(1+\tan\theta') \qquad (15)$$

and ψ_1 and ψ_2 are equivalent orbitals with their charge clouds extending along two straight lines which make an angle θ' with the x- and y-axis, respectively. In these orbitals (14), the coefficients of $x-y$ are also independent of the bond angle or the angle between the directions of their charge clouds. It is of interest to see that the LCAO-SCF calculation comes to the same conclusion for the coefficient of $x-y$ as the electron pair bond theory.

The localized symmetry orbitals of the NH_2 radical can be obtained by a unitary transformation of the two of the a_1 orbitals as shown by Pople[20] in the case of H_2O, and they are given in Table II. In these orbitals, $1a_1'$ and $2a_1'$ may be said to represent the a_1 lone pair and the a_1 bonding orbital, respectively. It is evident that the lone pair orbital $1a_1'$ has mainly s character, especially at the bond angle of 90°, but has not a perfect s character as it has in the electron pair bond theory, and the relationship between the coefficients of s and $x+y$ is also complicated. This may be due to the influence of ionic character.

TABLE II

LOCALIZED SYMMETRY ORBITALS FOR THE $^2B_1$ STATE

$$K(a_1)=n$$

$$1a_1'=\begin{pmatrix}0.975\\0.953\\0.920\\0.740\\0.000\end{pmatrix}(s)-\begin{pmatrix}0.159\\0.214\\0.277\\0.476\\0.707\end{pmatrix}(x+y)$$

$$2a_1'=\begin{pmatrix}-0.113\\-0.038\\+0.049\\+0.360\\+0.737\end{pmatrix}(s)+\begin{pmatrix}0.531\\0.535\\0.533\\0.464\\0.000\end{pmatrix}(x+y)+\begin{pmatrix}0.290\\0.290\\0.289\\0.256\\0.211\end{pmatrix}(h+h')$$

$$1b_1=z$$

$$1b_2=\begin{pmatrix}0.397\\0.389\\0.386\\0.385\\0.392\end{pmatrix}(x-y)+\begin{pmatrix}0.532\\0.503\\0.479\\0.449\\0.431\end{pmatrix}(h-h')$$

at the bond angle of $\begin{pmatrix}90°\\115°\\120°\\150°\\180°\end{pmatrix}$, respectively.

The "LCAO orbital energies" represent good approximation to the ionization energies of corresponding electron shells. In the present work, the calculated value of $2a_1$ orbital is 14.4 ev which is the minimum ionization energy at the equilibrium bond angle for the $^2B_1$ state. This value approximately corresponds to the removal of an electron from $2a_1$ orbital, but it is somewhat higher than the observed one of 11.05 ev.[21]

In spite of the fact that both the $2a_1$ and $1b_1$ orbitals turn into the $1\pi_u$ orbital in the linear form, the ionization energy of $2a_1$ is lower than that of $1b_1$, and neither value shows the same value at the bond angle of 180° in Fig. 2. This is due to the fact that the NH_2 radical has an unpaired electron: the $2a_1$ orbital is filled by two electrons with paired spins while the $1b_1$ has only one electron, and further the electronic repulsion in the former is stronger than in the latter. In view of these facts, the ground state of the CH_2 radical is probably the $^3B_1$ state, for the energy of the $^1A_1$ state $(1a_1)^2(1b_2)^2(2a_1)^2$ is considered to be higher than that of the B_1 states $(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1$ and also the $^3B_1$ state may be the most stable.

Using the LCAO MO's in Table I without configuration interaction, the dipole moment for the corresponding bond angle can be calculated and is shown in Table III. These values may be rather small but not considered to be unreasonable as compared with the value of the ammonia molecule of 1.40 D.[22] This correspondence may be due to the similarity of electronic structures between the NH_2 radical and the ammonia molecule. But such correspondence does not exist in the relationship between the CH radical and the methane molecule, for there is a consi-

TABLE III

DIPOLE MOMENT

Bond angle	90°	105°	120°	150°	180°
Dipole moment D. ($N^-H_2^+$)	1.75	1.32	0.83	−0.14	0.00

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[19] For example, see T. Inui and S. Yanagawa, "Group Representation and Atoms and Molecules", Shokabo, Tokyo, (1950) p. 253.

[20] J.A. Pople, *J. Chem. Phys.*, 21, 2234 (1953).

[21] J.C. Devins and M. Burton *J. Am. Chem. Soc.*, 76, 2618 (1954).

[22] L.G. Wesson, "Table of Electric Dipole Moments", The Technology Press. Massachusetts Institute of Technology, (1948) p. 2.

derable difference in the electronic structure, that is, the former has lone pair electrons but the electrons in the latter are all bonding[5], and the lone pair electrons make a substantial contribution to the dipole moments[23].

Electronic States and Structures

By using the LCAO MO's given in Table I, the energies of the lower electronic states were calculated without configuration interaction, and are shown in Fig. 3. They may be considered to be fairly reasonable, if the good result of the CH radical[5] obtained by the similar procedure is referred to. The electronic configurations of these states are as follows:

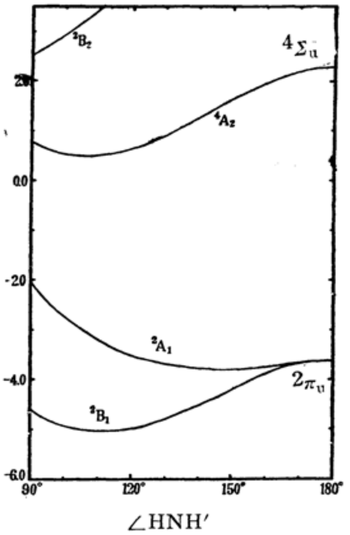

Fig. 3. Lower electronic states of the free NH_2 radical (without configuration interaction). The origin of energy is chosen to be $N(^4S)+2H(^2S)$.

$^2B_1$: $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^1$
$^2A_1$: $K(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^2$
$^4A_2$: $K(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1(2b_2)^1$
$^2B_2$: $K(1a_1)^2(1b_2)^1(2a_1)^2(1b_1)^2$.

Herzberg[24] showed that, in the upper state of the α bands, the bond angle is fairly large and possibly 180° while, in the lower state, it has an intermediate value. According to Luft's estimation,[25] the equilibrium bond angles of the lower and the upper state are 110° and 135-160°, respectively. These results are very close to the values of the present calculation for the $^2B_1$ and the $^2A_1$ state. The calculated value of a $^2B_1 \rightarrow {}^2A_1$ transition (1.8 ev) is also in fairly good agreement with the experimental result, which was observed in absorption spectrum in the region of 4500–7400 Å. In view of these facts, the present calculation may be said to give the theoretical interpretation of the α bands as follows: this spectrum is due to the free NH_2 radical, and the upper and the lower states are the $^2A_1$ and the $^2B_1$ state, respectively.

The calculated $^2B_2$ state was, however, higher than that predicted by Mulliken[4]. This is mainly due to the facts that the present calculation ignores configuration interaction and that the variational procedure is carried out for the $^2B_1$ state only. Especially, the second $^2B_2$ state $K(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^1$ is very close to the lowest $^2B_2$ state, and then the effect of configuration interaction may not be disregarded.

In the previous section, the similarity of electronic structures for the nitrogen atoms in the NH_2 radical and in the ammonia molecule has been discussed from the point of view of dipole moment. Besides this, such similarity can be deduced from their structures, that is, the tetrahedral structure of bond angle is almost perfectly preserved in the ground state of the NH_2 radical as in the ammonia molecule. On the other hand, the HCO angle of the HCO radical is also scarcely changed from that of the formaldehyde molecule in the photochemical reaction,[26] and this may be also due to the preservation of the electronic structure for the carbon atom. In view of these facts, the bond angle of the ground state may scarcely be changed in such reactions due to the preservation of electronic structure for the atom whose bond is ruptured. In the excited states, however, such property is not preserved in the case of the NH_2 radical and of the HCO radical. The analogous relationship between the ground and the excited state can be seen in molecules such as HCN[27], C_2H_2[28] and others, in which the linear form is not preserved in the excitation of an electron from the bonding orbital to the non- or anti-bonding orbital.

The results in the present work are, however, qualitatively satisfying, but can not be conclusive because of the method used, the approximate values in the many-center integrals and the ignorance of configuration interaction. It may be desiable to investigate these points more accurately, though they, in part, have been discussed by the present author in his calculation of CH[5].

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[23] A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

[24] G. Herzberg, private communication.

[25] N.W. Luft, *Discussion Faraday Soc.*, No. 14, 114 (1952).

[26] D.A. Ramsay, *J. Chem. Phys.*, **21**, 960 (1953).

[27] G. Herzberg and K.K. Innes, to be published.

[28] C. W. King and C. K. Ingold, *Nature*, **169**, 1101 (1952); K. K. Innes, *J. Chem. Phys.*, **22**, 863 (1954).

Summary

LCAO MO's and ionization potentials have been calculated for the ${}^2B_1$ state of the free NH_2 radical by using the LCAO-SCF method. The interactions of all electrons have been explicitly considered, but the orthogonal relationship between the 1*s* orbitals of nitrogen and hydrogen was assumed. Using these MO's the lower electronic states have also been investigated without configuration interaction. The calculated value of a ${}^2B_1 \rightarrow {}^2A_1$ transition is 1.8 ev in fairly good agreement with the observed one of the α bands of ammonia in the region of 4500 to 7400 Å. The calculated bond angles of the ${}^2B_1$ and the ${}^2A_1$ state are about 110° and 150°, respectively. These results are in good agreement with the observation and the opinion by Herzberg and Ramsay and the estimation by Luft.

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