Primary Process in Photochemical Decomposition of AH_N-Type Molecules

By Jiro HIGUCHI

(Received December 6, 1956)

1. Introduction

Photochemical reactions have in general been discussed in the classification of the primary process and the succeeding secondary process. The latter process is concerned in the reaction of free radicals, and is essentially a problem of chemical kinetics. On the other hand, the detailed study of the primary process requires the knowledge concerned with the electronic structures of the molecules and the free radicals produced. Above all, the full comprehension of the nature of each orbital is necessary to discuss the properties of these electronic states, and particularly of the potential energy surfaces, which are closely connected with the primary process. Unfortunately, such a knowledge has scarcely ever been obtained from experiments, except for a few simple molecules, due to the difficulty of the spectroscopic analysis for polyatomic molecules and for free radicals. Accordingly, the theoretical investigation is of great significance for such problems. Another theoretically important known fact is the adiabatic correlation rule, which has been developed by Wigner and Witmer[1], by Mulliken[2] and by Shuler[3]. The rule must be taken into consideration for the polyatomic system, although occasionally it is not so effective for intermediates of low symmetry, because there are few restrictions on the correlations of the states between reactants and products. Other theoretical considerations may be of minor importance for qualitative discussions. However, it goes without saying that the experimental facts play the conclusive part of the present discussion.

In the present paper, the primary process of photochemical decomposition in the first absorption region will be taken up for AH_N-type (A denotes atoms like C, N, O and others; and $N=4,3,2$) molecules from the viewpoint of the molecular orbital theory. The experimental investigations of these reactions have long been done by many authors[4], and the electronic spectra of these molecules have also been observed[4-6]. On the other hand, the theoretical investigations of some of these electronic structures have recently been done with fruitful results by several authors[7-11]. Accordingly, these reactions may be said to be one of the most suitable examples in studying the photochemical primary process.

2. General Consideration

Electronic Structure.—Before discussing the primary process, it is convenient to explain briefly the common electronic properties of the AH_N molecules and the free AH_{N-1} radicals. For the ground state, the electron configuration of an AH_N molecule can in general be given by $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)^2$, in which K is the inner-shell of the molecule, nearly the same as that of the A atom, and ϕ_i's are the molecular orbitals mainly built from the valence-shell electrons of the constituent atoms in the LCAO-MO approximation. The sufficies of these MOs are chosen in the order of increasing energy. The lowest vacant orbital is ϕ_5 with the total symmetry A_1 and the structure of the first excited state is $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)(\phi_5)$. The ϕ_5 orbital has been considered to be of a considerable $(n+1)s$ orbital character of the A atom, n being the principal quantum number of the valence-shell electron.

---

[1] E. Wigner and E. E. Witmer. *Z. Physik*, **51**, 859 (1928).

[2] R. S. Mulliken, *Phys. Rev.*, **43**, 279 (1933).

[3] K. E. Shuler, *J. Chem. Phys.*, **21**, 624 (1953).

[4] For example, see G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc. New York (1939), and W. A. Noyes, Jr. and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York (1941).

[5] H. Sponer, "Molekülspektren und ihre Anwendung auf chemische Probleme," Verlag Julius Springer, Berlin (1935), I. Tabellen, p. 97.

[6] H. Sponer and E. Teller, *Revs. Modern Phys.*, **13**, 75 (1941).

[7] A. D. Walsh, *J. Chem. Soc.*, **1953**, 2260.

[8] A. D. Walsh, ibid., 2296.

[9] R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 887 (1955).

[10] F O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955).

[11] J. Higuchi, *J. Chem. Phys.*, **24**, 535 (1956).

TABLE I

MOLECULAR ORBITALS OF AH_N MOLECULES AND THEIR BONDING POWER

	T_d (AH_4)	
ϕ_1	$1a_1$	Strong-bonding
ϕ_2 ϕ_3 ϕ_4	$1t_2$	Strong-bonding
ϕ_5	$2a_1$	Non-bonding
ϕ_r	ra_1	Rather strong-antibonding

	D_{3h} (AH_3)	
ϕ_1	$1a_1'$	Strong-bonding
ϕ_2 ϕ_3	$1e'$	Strong-bonding
ϕ_4	$1a_2''$	Non-bonding
ϕ_5	$2a_1'$	Non-bonding
ϕ_r	ra_1'	Rather strong-antibonding

	C_{3v} (AH_3)	
ϕ_1	$1a_1$	Strong-bonding
ϕ_2 ϕ_3	$1e$	Strong-bonding
ϕ_4	$2a_1$	Weak-bonding
ϕ_5	$3a_1$	Non-bonding
ϕ_r	ra_1	Strong-antibonding

	C_{2v} (AH_2)	
ϕ_1	$1a_1$	Strong-bonding
ϕ_2	$1b_2$	Strong-bonding
ϕ_3	$2a_1$	Weak-bonding
ϕ_4	$1b_1$	Non-bonding
ϕ_5	$3a_1$	Non-bonding
ϕ_r	ra_1	Strong-antibonding

	$D_{\infty h}$ (AH_2)	
ϕ_1	$1\sigma_g$	Strong-bonding
ϕ_2	$1\sigma_u$	Strong-bonding
ϕ_3 ϕ_4	$1\pi_u$	Non-bonding
ϕ_5	$2\sigma_g$	Non-bonding
ϕ_r	$r\sigma_g$	Rather strong-antibonding

	$C_{\infty v}$ (AH)	
ϕ_1	1σ	Strong-bonding
ϕ_2	2σ	Weak-bonding
ϕ_3 ϕ_4	1π	Non-bonding
ϕ_5	3σ	Non-bonding
ϕ_r	$r\sigma$	Strong-antibonding

On the other hand, the LCAO-MO calculation of the AH_N molecule gives the strong-antibonding a_1 orbital ϕ_r, which may correspond to the ϕ_5 orbital, by taking the *ns* and *np* of the A atom and the 1*s*'s of the H atoms into account. As discussed by Mulliken[12], however, the strong-antibonding orbital ϕ_r is not so good an approximation of the ϕ_5 orbital as compared with the $(n+1)s$ orbital of the A atom. It is noted that one higher strong-antibonding orbital is also expected instead of the above antibonding orbital, even if the $(n+1)s$ orbital is taken into account, because of the fairly large overlap between the $(n+1)s$ orbital of the A atom and the 1*s* orbital of the H atom. In that case, a more satisfactory approximation of the ϕ_5 orbital will be obtained with the better repulsive orbital ϕ_r. In the present paper, however, the ϕ_i $(i \leqq 4)$ and ϕ_r orbitals will be considered as linear combinations of *ns*, *np* orbitals of A atom and 1*s*'s of H atoms, and the properties on the ϕ_5 orbital will be discussed in taking the interaction with the ϕ_r orbital into account[13]. In such an argument, the repulsive state with configuration $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)(\phi_r)$ may be a rather high location near the equilibrium structure. In a similar way, the electronic structures of the ground and the first excited state of a free AH_{N-1} radical can be represented by respectively $K'(\phi_1')^2(\phi_2')^2(\phi_3')^2(\phi_4')$ and $K'(\phi_1')^2(\phi_2')^2(\phi_3')(\phi_4')^2$ or $K'(\phi_1')^2(\phi_2')^2(\phi_3')^2(\phi_5')$, in which the dashes are given in order to distinguish that it is a free radical.

Actually, the stable structures of the AH_4, AH_3 and AH_2 molecules discussed here are respectively tetrahedral, pyramidal and isosceles triangle, the symmetry of which are T_d, C_{3v} and C_{2v} respectively. By taking the order of the increasing energy, the MOs ϕ_i's for each symmetry and the common bonding power near the equilibrium form can be listed as given in Table I. As can be seen from there, the bonding power of the ϕ_5 orbital of AH_N molecules can generally be shown as non-bonding and the difference is not great. But that of the ϕ_4 is somewhat different one to the other, and decreases with decreasing number of hydrogen atoms. This is one reason why the nature of the first excited state cannot be determined simply.

Potential Energy Surface.—Considering the property of ϕ_5 orbital, the first excited state $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)(\phi_5)$ has rather less bonding property than the ground state, since the bonding power of the ϕ_4 orbital is at least not as weak as

---

[12] R. S. Mulliken, *J. Chem. Phys.*, 3, 517 (1935).

[13] The forms of the ϕ_i $(i \leqq 4)$ orbitals are scarcely changed at all by including the $(n+1)s$ orbital of A atom and the higher orbitals (J. Higuchi, unpublished work).

compared with the ϕ_5 orbital. In the approximation of single configuration, therefore, this state is not repulsive and may reach the excited doublet state $K'(\phi_1')^2(\phi_2')^2(\phi_3')(\phi_4')(\phi_5')$, or $K'(\phi_1)^2(\phi_2')^2(\phi_3')^2(\phi_5')$, of the free AH_{N-1} radical and the $1s\ ^2S$ state of the H atom by increasing one of the AH internuclear distances. The above doublet state of the AH_{N-1} radical, however, is in a rather high location as compared with the ground state $K(\phi_1')^2(\phi_2')^2(\phi_3')^2(\phi_4')$, since the ϕ_5' orbital has also a considerable $(n+1)s$ orbital character. In such a single configurational approximation, therefore, the fact that the first excited state of the AH_N molecule leads to decomposition cannot be explained.

The energy of the repulsive orbital ϕ_r is, however, rapidly lowered with increasing one of the AH internuclear distances because of the decrease of the overlap integrals, and so the ϕ_r orbital becomes the fifth orbital on the energetic ground. In the present paper, however, for convenience the sufficies i's are not changed at larger AH internuclear distances. Accordingly, some repulsive state $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)(\phi_r)$ exists, which may reach the ground state $K'(\phi_1')^2(\phi_2')^2(\phi_3')^2(\phi_4')$, or the first excited state $K'(\phi_1')^2(\phi_2')^2(\phi_3')(\phi_4')^2$, of the AH_{N-1} radical. However, this repulsive state has the same symmetry as that of the first excited state $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)(\phi_5)$, and the former potential energy surface crosses that of the latter one near a somewhat larger AH internuclear distance in the single configurational approximation. In view of these facts, it is possible that the AH_N molecule decomposes to give the free AH_{N-1} radical and the H atom beyond the crossing curve between the above-mentioned potential energy surfaces.

Primary Process.—In general, no electronic spectrum of the AH_N molecule exists up to comparatively short wave-lengths, occasionaly until the Schumann region[4-6]. The first absorption spectrum of the AH_N molecule occurs as a continuum or as diffuse bands and is presumed to occur because of the transition from the ϕ_4 orbital to the ϕ_5 orbital. By absorbing the light of this region, the molecules are generally excited to the above-mentioned first excited singlet state, which is the lowest member of the Rydberg series of the molecule. The excited molecule dissociates to the ground, or the first excited, state of AH_{N-1} radical and the ground state $1s\ ^2S$ of H atom due to some of the AH stretching vibrations, beyond the crossing point between the first and the repulsive excited states. In this case, the shape of the potential energy surface of the first excited state differs from one molecule to the other, and so the condition of the photochemical decomposition is not always quite the same. However, it may be noted that the following rules are valuable to discuss the types of photochemical decomposition in the first absorption region.

(1) The first absorption spectrum is continuous, if the highest occupied orbital ϕ_4 is considerably strong-bonding.

(2) In the case of the highest occupied orbital ϕ_4 being not so strong-bonding, the type of the first absorption spectrum is determind from the antibonding property of the first excited state due to the interaction between the lowest vacant orbital ϕ_5 and the strong-antibonding orbital ϕ_r. In this case, (2a) the spectrum may be diffuse, if the ϕ_r orbital is not so strong-antibonding; (2b) the spectrum may be continuous, if the ϕ_r orbital is considerably strong-antibonding.

The reason for this can be explained as follows: in the case of (1) the AH equilibrium bond distance in the first excited state is fairly lengthened, and so the crossing may take place near the equilibrium internuclear distance of this state. Since the first and the repulsive state have the same symmetry, the actual potential energy curve to this decomposing direction may not have a maximum point. Accordingly, the decomposition in the first excited state takes place very easily by some of the AH stretching vibrations and the first absorption spectrum occurs as a continuum. In the case of (2a), however, the equilibrium internuclear distance in the first excited state is not so large that the crossing may take place at a somewhat larger AH internuclear distance than the equilibrium one. Accordingly, the actual potential energy curve to this decomposing direction may have a maximum point and the first absorption spectrum occurs as diffuse.

These rules, however, are also not useful to determine the state of the decomposed free AH_{N-1} radical, when its many states are lower than the first excited state of the AH_N molecule. In this case, certainly the adiabatic correlation rule occasionally plays some important role, but generally is not useful because of the lowering of symmetry for the intermediate. For the determination of the states of products, therefore, it may be safe to investigate each molecule, at least to make a distinction of the molecule according to its symmetry, as will be discussed in the following chapters.

3. Primary Process in Photochemical Decomposition of AH_4 Molecules

The photolysis of the AH_4 molecule, such as CH_4, SiH_4, GeH_4, etc., has been investigated by several authors, but the works except for the CH_4 molecule are very few[4]. The first absorption of the molecules occurs as continuum below about 1600 Å, but no bands have been observed[4,5]. The primary process in photochemical decomposition by this absorption has been considered as follows:

$$AH_4 + h\nu \longrightarrow AH_3 + H,$$

although the other process has also been considered in shorter wave-lengths[4].

Electronic Structure.—The AH_4 molecule has tetrahedral symmetry T_d and the electron configuration of the ground state ${}^1A_1$ is $K(1a_1)^2(1t_2)^6$, and that of the first excited states ${}^{1,3}T_2$ is $K(1a_1)^2(1t_2)^5(2a_1)$. The $1a_1$ and the $1t_2$ orbitals are strong-bonding, while the $2a_1$ orbital is nearly non-bonding and has $(n+1)s$-like property of the A atom. Accordingly, the equilibrium bond distance of the ${}^{1,3}T_2$ states may be lengthened as compared with that of the ground state ${}^1A_1$, because of the excitation from the strong-bonding orbital $1t_2$ to the nearly non-bonding orbital $2a_1$. As discussed in the previous chapter, however, the molecule has a higher antibonding orbital ra_1, and so the repulsive ${}^3T_2$ state $K(1a_1)^2(1t_2)^5(ra_1)$ is also expected.

On the other hand, the AH_3 radical may be low-pyramidal with symmetry C_{3v} (or may occasionally be planar with symmetry D_{3h}). The electron configuration of the ground state ${}^2A_1$ (or ${}^2A_2''$) is $K(1a_1)^2(1e)^4(2a_1)$ (or $K(1a_1')^2(1e')^4(1a_2''))$, and the $1a_1$ (or $1a_1'$) and the $1e$ (or $1e'$) orbitals are strong-bonding, while the $2a_1$ (or $1a_2''$) orbital is weak-bonding (or non-bonding). The excited states of the AH_3 radical also exist, for example, ${}^2E$ $K(1a_1)^2(1e)^3(2a_1)^2$ (or ${}^2E'$ $K(1a_1')^2(1e')^3(1a_2'')^2$) and ${}^2A_1$ $K(1a_1)^2(1e)^4(3a_1)$ (or ${}^2A_1'$ $K(1a_1')^2(1e')^4(2a_1')$), but they are rather high as compared with the first excited state of the corresponding AH_4 molecules as shown in Fig. 1. Accordingly, they are not responsible for this reaction and need not be discussed in detail.

TABLE II
CORRELATION BETWEEN REPRESENTATIONS OF GROUPS $T_d-C_{3v}-D_{3h}$

T_d	C_{3v}	D_{3h}
A_1	A_1	A_1', A_2''
A_2	A_2	A_2', A_1''
E	E	E', E''
T_1	A_2, E	A_2', A_1'', E', E''
T_2	A_1, E	A_1', A_2'', E', E''

Potential Energy Surface.—The correlation between representations of groups $T_d-C_{3v}-D_{3h}$ is given in Table II. By increasing one of the AH internuclear distances, the first excited states ${}^{1,3}T_2$ of the AH_4 molecule with symmetry T_d reaches the ${}^2A_1$ state $K(1a_1)^2(1e)^4(3a_1)$ (or ${}^2A_1'$ $K(1a_1')^2(1e')^4(2a_1')$) of the AH_3 radical with symmetry C_{3v} (or D_{3h}) and the ${}^2S$ state of the H atom, passing through the ${}^{1,3}A_1$ state $K(1a_1)^2(1e)^4(2a_1)(3a_1)$ of the intermediate AH_4 with symmety C_{3v}, in the approximation of single configuration. But the repulsive excited state ${}^3T_2$ of the AH_4 molecule reaches the ground state ${}^2A_1$ (or ${}^2A_2''$) of the AH_3 radical and the ${}^2S$ state of the H atom[14]. The first and the repulsive excited states of the AH_4 molecule, however, have the same symmetry T_2 and so their interaction is not so weak. Furthermore, the equilibrium bond distance of the first excited state is fairly

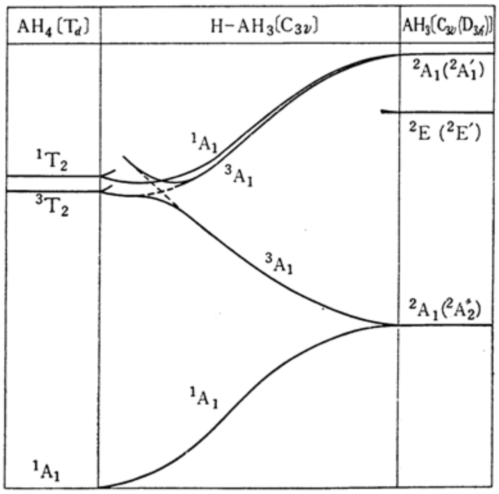

Fig. 1. Potential energy curves for photochemical decomposition of AH_4 molecule. The relative energy scale of the right and the left part was chosen to fit the CH_4 molecule and the CH_3 radical.

---

[14] The instability of the ${}^{1,3}T_2$ states can also be supposed from the Jahn-Teller effect.

large, and the variation of energy by changing the AH internuclear distance may be small in this region. Accordingly, the actual potential energy curve of the first excited state ${}^3T_2$ to the ${}^2A_1$ state of the AH_3 radical may not have a maximum point as shown in Fig. 1[15]. As the result of this, the first absorption spectrum of the AH_4 molecule occurs as a continuum (case (1) of the rule in Chapter 2).

Primary Process.—In the AH_4 molecule, the influence of vibration is not important because the first excited states ${}^{1,3}T_2$ electronically correlate to the ${}^2A_1$ (or ${}^2A_2''$) state of the AH_3 radical and the ${}^2S$ state of the H atom[16]. It may, therefore, be most convenient to explain the mechanism from the electronic and energetic viewpoints. That is, the AH_4 molecule absorbing the wave-length of about 1600 Å is excited to the first ${}^1T_2$ state[17]. The excited molecule dissociates to the ${}^2A_1$ (or ${}^2A_2''$) state of the free AH_3 radical and the 1*s* ${}^2S$ state of the H atom due to the singlet-triplet transition and to some of the AH stretching vibration, passing through the intermediate with symmetry C_{3v} as shown in Fig. 1. In the meanwhile, the bond angle of ∠HAH′ may gradually be increased by the action of the AH bending vibration. The electronic property of the highest singly occupied orbital also changes from $(n+1)s$-like nearly non-bonding to strong-antibonding beyond the above-mentioned crossing point. The process passing through the other structures of the intermediates can also be considered. That is, it may be probable that one of the H atoms is slightly displaced from the trigonal axis in the excited state. Certainly, the process passing through this intermediate is not contradictory to the adiabatic correlation rule, and the potential energy curve and the electronic property in such a possible process are generally similar to those in the above-mentioned case. Accordingly, such processes are not discussed here in detail.

4. Primary Process in Photochemical Decomposition of AH_3 Molecules[18]

The photolysis of the NH_3 molecule has long been investigated by many authors, and that of the PH_3, AsH_3 and SbH_3 molecules has also been studied by several authors[4]. The first absorption spectrum of the NH_3 and the PH_3 molecules begins at about 2300 Å as diffuse bands, but that of the AsH_3 and the SbH_3 molecules appears to be continuous below about 2400 Å[4,5]. The primary process in the photochemical decomposition by this absorption has generally been considered to be predissociation:

$$AH_3 + h\nu \longrightarrow AH_3^* \longrightarrow AH_2 + H.$$

Electronic Structure.—The AH_3 molecule has pyramidal symmetry C_{3v} and the electron configuration of the ground state ${}^1A_1$ (or ${}^1A_1'$ for the symmetry D_{3h}) is $K(1a_1)^2(1e)^4(2a_1)^2$ (or $K(1a_1')^2(1e')^4(1a_2'')^2$). The $1a_1$ (or $1a_1'$) and the $1e$ (or $1e'$) orbitals are strong-bonding, while the $2a_1$ (or $1a_2''$) orbital is weak-bonding (or non-bonding) and its bonding power increases with decreasing bond angle of ∠HAH′. In the ground state of the PH_3, AsH_3 and SbH_3 molecules, the equilibrium bond angles decrease owing to the increase of the *nd*-orbital character of A atom[9,19], and the bonding power of the $2a_1$ orbital increases. As the results of this, the potential barrier of inversion increases with increasing the molecular weight of the AH_3 molecule[20].

The lowest vacant orbital $3a_1$ (or $2a_1'$) is nearly non-bonding and has $(n+1)s$-like property of the A atom, while the ra_1 (or ra_1') is strong-antibonding and the antibonding power increases with decreasing the bond angle ∠HAH′[21]. In the first excited states ${}^{1,3}A_1$ $K(1a_1)^2(1e)^4(2a_1)(3a_1)$ (or ${}^{1,3}A_2''$ $K(1a_1')^2(1e')^4(1a_2'')(2a_1')$), the equilibrium AH bond distance is somewhat lengthened and the equilibrium bond

---

[15] In this case, the first excited singlet state ${}^1T_2$ does not reach the ground state ${}^2A_1$ of AH_3 from the atomic orbital consideration in the infinite internuclear separation between the AH_3 and the H.

[16] The AH_4 molecule with symmetry T_d has nine fundamental vibrations: one with species a_1, one doubly degenerate frequencies with species e and two triply degenerate ones with species t_2. For the electronically excited ${}^{1,3}T_2$ states, therefore, the corresponding vibronic states to one of the AH stretching vibrations are ${}^{1,3}T_2 \times A_1 = {}^{ev1,3}T_2$ and ${}^{1,3}T_2 \times T_2 = {}^{ev1,3}A_1 + {}^{ev1,3}E + {}^{ev1,3}T_1 + {}^{ev1,3}T_2$ (In the present paper, only the species symbols for the vibronic states are prefixed by a left superscript ^{ev} to avoid confusion to the electronic states.) Accordingly, all the species come into question and therefore the vibronic correlation rule is not especially important to determine this primary process.

[17] The possibility of the excitation to the first triplet state also exists, but may be fairly small as compared with that to the first excited singlet state.

[18] Preliminary report on the NH_3 molecule was given in *Proc. Japan Acad.*, **32**, 276 (1956).

[19] This decrease is also due to the considerably larger sizes of atoms, P, As and Sb, than the N atom (See, Ref. 9).

[20] A. Gilchrist and L. E. Sutton, *J. Phys. Chem.*, **56**, 319 (1952).

[21] This is due to the increase of *s*-*p* hybridization in the ϕ_r orbital, the coefficients of which have opposite signs to those of the 1*s*′s of H atoms. (See, Ref. (11)).

angle ∠HAH′ increases as compared with that of the ground state, since the one electron excitation from the weak-bonding $2a_1$ orbital decreases the power of bonding and also of pyramidalization. In fact, the first excited state of the NH_3 molecule is planar[11] and that of the other molecules are also expected to have a fairly large equilibrium bond angle.

On the other hand, the AH_2 radical is an isosceles triangle with symmetry C_{2v}. The ground state is the $^2B_1$ $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)$ and the first excited state is the $^2A_1$ $K(1a_1)^2(1b_2)^2(2a_1)(1b_1)^2$. The energy separation between these states is not so large, for example, less than 2 eV for the NH_2 radical[22]. The $1a_1$ and the $1b_2$ orbitals are strong-bonding and the $2a_1$ orbital is weak-bonding but the $1b_1$ orbital is non-bonding, The higher excited states of the radical also exist, but they are high location as compared with the first excited states $^{1,3}A_1$ (or $^{1,3}A_2''$) of the corresponding AH_3 molecule. Accordingly, they are not responsible for this reaction and need not be discussed in detail.

Potential Energy Surface.—To discuss the potential energy surfaces, it is convenient to make a distinction between the process passing through the planar intermediate and the others, since the most stable structure of the first excited states are planar and the correlation between the planar molecules is characteristic. Accordingly, the correlations between representations of groups in Table III are separately given for $C_{3v}-D_{3h}-C_{2v}$ and $C_{3v}-C_s-C_{2v}$.

TABLE III

CORRELATION BETWEEN REPRESENTATIONS OF GROUPS $C_{3v}-D_{3h}-C_{2v}$ and $C_{3v}-C_s-C_{2v}$

C_{3v}	D_{3h}	C_{2v}
A_1	A_1' A_2''	A_1 B_1
A_2	A_2' A_1''	B_2 A_2
E	E' E''	A_1, B_2 A_2, B_1

C_{3v}	C_s	C_{2v}
A_1	A'	A_1, B_1
A_2	A''	A_2, B_2
E	A', A''	A_1, A_2, B_1, B_2

For the planar AH_3 molecule with symmetry D_{3h}, the first excited states decompose to AH_2+H passing through the intermediate AH_3 molecule with symmetry C_{2v}. As can be seen from Table III, the ground state $^1A_1'$ $K(1a_1')^2(1e')^4(1a_2'')^2$, the first excited states $^{1,3}A_2''$ $K(1a_1')^2(1e')^4(1a_2'')(2a_1')$ and the repulsive excited states $^{1,3}A_2''$ $K(1a_1'')^2(1e')^4(1a_2'')(\mathrm{r}a_1')$ of AH_3 with symmetry D_{3h} correspond to respectively the ground states $^1A_1$ $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^2$, the first excited states $^{1,3}B_1$ $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)(3a_1)$ and the repulsive excited states $^{1,3}B_1$ $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)(\mathrm{r}a_1)$ of AH_3 with symmetry C_{2v}. As shown in Fig. 2, on stretching one AH bond distance, the ground state $^1A_1'$ becomes gradually unstable, and dissociates to the $^2A_1$ state of the AH_2 radical. Similarly, the first excited states $^{1,3}A_2''$ are also elevated and reach the second $^2B_1$ (or $^4B_1$) state $K(1a_1)^2(1b_2)^2(2a_1)(1b_1)(3a_1)$ of the AH_2 radical. On the other hand, the repulsive excited states $^{1,3}A_2''$ are continuously lowered with increasing one AH bond distance and dissociate to the ground state $^2B_1$. It is, however, noted that in the first excited states the difference of the equilibrium bond distance from the ground state is not much great, since the ϕ_4 orbital is the non-bonding $1a_2''$ and the antibonding property due to the interaction between the $2a_1'$ and the $\mathrm{r}a_1'$ orbital is rather weak because of no *p*-character in these orbitals. This makes possible the large deviation between the internuclear separation of the first excited state in equilibrium and that of the corresponding crossing point, and also makes possible the fairly large energy difference between these points. Accordingly, a maximum point exists in each actual potential energy curve of the first $^{1,3}B_1$ states as shown in Fig. 2, and the first absorption spectrum appears as diffuse in this process (case (2a) of the rule in Chapter 2, for example,

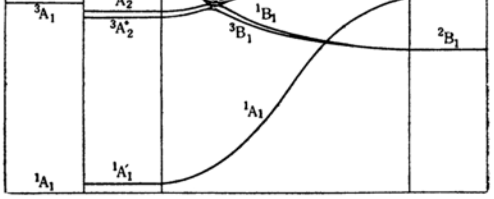

Fig. 2. Potential energy curves for photochemical decomposition of AH_3 molecule passing through the planar intermediate. The relative energy scale of the right and the left part was chosen to fit the NH_3 molecule and the NH_2 radical.

---

[22] G. Herzberg and D. A. Ramsay, *Discussions Fraday Soc.*, No. **14**, 11 (1952).

NH_3). At a fairly larger AH internuclear distance, the crossing between the ${}^{1,3}B_1$ states and the ${}^1A_1$ state also takes place, but their interactions need not be taken into consideration so greatly, because their symmetries are not the same.

For pyramidal AH_3 molecule with symmetry C_{3v}, the molecule dissociates to AH_2+H passing through the intermediate AH_3 with symmetry C_s. Analogous relations also exist in this case as shown in Fig. 3. The first excited states ${}^{1,3}A_1$, however, may be somewhat stabilized with the small increase of one AH bond distance, since the $2a_1$ orbital is weak-bonding. Furthermore, the bonding power of the $2a_1$ orbital and the antibonding power of the ra_1 orbital increases with decreasing the bond angle of ∠HAH′, so that the stabilization by increasing one AH bond distance also increases[11]. Accordingly, the potential barrier in the crossing point of the first excited state ${}^3A'$ may be lowered and finally the potential energy curve may not have a maximum point at a bond angle smaller than a certain value. This tendency becomes strong with increasing molecular weight of the AH_3 molecule due to the stabilization of the $2a_1$ orbital under the influence of the *nd*-orbital character of the A atom in the molecule, and the first absorption spectrum appears as continuous (case (2b) of the rule in Chapter 2). Another difference from the planar molecule is the non-crossing between the ground state ${}^1A'$, which correlates with the ${}^1A_1$ state of C_{2v}, and the first excited singlet state ${}^1A'$, which correlates with the ${}^1B_1$ state of C_{2v}. Their symmetries are the same except for the symmetry C_{2v}, so that their interaction increases with decreasing the bond angle ∠HAH′. Consequently, the potential energy curve of the first excited singlet state ${}^1A_1$ of AH_3 reaches the ${}^2A_1$ state of AH_2. The first excited triplet state ${}^3A_1$, however, reaches the ${}^2B_1$ state of AH_2 passing through the intermediate with symmetry C_s, because of the difference in the spin multiplicities.

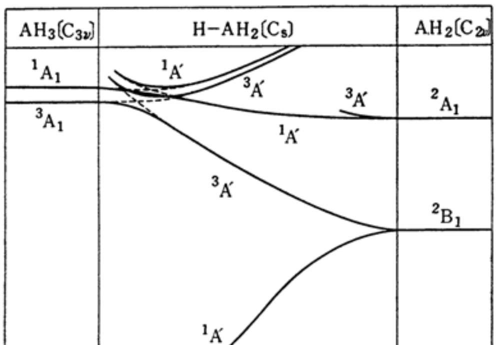

Fig. 3. Potential energy curves for photochemical decompostion of AH_3 molecule passing through the non-planar intermediate.

Primary Process.—In the primary process in photochemical decomposition, the AH_3 molecule in the ground state ${}^1A_1$ (or ${}^1A_1'$) absorbs the wave-length of about 2200 Å, and is excited to the first excited singlet state ${}^1A_1$. In the first excited states ${}^{1,3}A_1$, the planar molecule with symmetry D_3 is in general most stable, so that the probability of taking this shape is very large for light AH_3 molecules.

Few of the excited molecules return to the ground state and most of them decompose to the free AH_2 radical and the H atom due to some of the AH stretching vibrations. The AH_3 molecule with symmetry C_{3v} (or D_{3h}) has four fundamental vibrations: two with species a_1 and two doubly degenerate frequencies with species e (or one with species a_1', one with species a_2'' and two doubly degenerate frequencies with species e'). Accordingly, the mode of the AH stretching vibration has species a_1 (or a_1') or preferably e (or e'), and so the corresponding vibronic state, which arises from the excitation of such a vibrational mode, is ${}^1A_1\times A_1={}^{ev1}A_1$ (or ${}^1A_2''\times A_1'={}^{ev1}A_2''$) or preferably ${}^1A_1\times A_1={}^{ev1}E$ (or ${}^1A_2''\times E'={}^{ev1}E''$).

When the planar molecule with symmetry D_{3h} has been realized, this electronically excited state correlates with the ${}^{ev1}B_1$ state or the ${}^{ev1}B_1$ and ${}^{ev1}A_2$ states of the intermediate AH_3 molecule with symmetry C_{2v}. On the other hand, the free AH_2 radical with symmetry C_{2v} has three fundamental vibrations: two with species a_1 and one with species b_2. Therefore, the corresponding vibronic states are ${}^2B_1\times A_1={}^{ev2}B_1$ and ${}^2B_1\times B_2={}^{ev2}A_2$ to the electronic ${}^2B_1$ state and are ${}^2A_1\times A_1={}^{ev2}A_1$ and ${}^2A_1\times B_2={}^{ev2}B_2$ to the electronic ${}^2A_1$ state. Besides this, the electronic state of the H atom in question is $1s\ {}^2S$. This means that in this case the restriction between these electronic states is not changed by the influence of vibration. For the excited AH_3 molecule with symmetry D_{3h}, therefore, the decomposition takes place passing through the potential energy curve shown in Fig. 2, and the products are the ${}^2B_1$ state of AH_2 and the ${}^2S$ state of H, but are not the ${}^2A_1$ state of AH_2 and the ${}^2S$ state of H. In the meanwhile, the bond angle of ∠HAH′ may be changed by the action of the AH bending vibration from 120° to a somewhat small angle, for example 103° for NH_2[23]. On the other hand, the possibility of the process passing through the triplet state may generally be very small because of the inhibition by the spin correlation rule.

Especially for the heavy AH_3 molecules, the planar first excited state is not necessarily realized and the decomposition may take place passing through the intermediate with symmetry C_s, because the equilibrium bond angle of these molecules is nearly 90° in the ground state. In this case, the influence of vibration may not be so important, since both the first excited states ${}^{1,3}A_1$ of AH_3 are possible to correlate electronically to both the ${}^2B_1$ and ${}^2A_1$ states of AH_2[24]. Consequently, in the case of the decomposition passing through the intermediate with symmetry C_s, the state of product AH_2 cannot be determined from the adiabatic correlation rule. It can, however, be said that the probability of the product being ${}^2B_1$ state may decrease with decreasing the bond angle of the AH_3 molecule. It is also noted that the process passing through the singlet-triplet transition mainly reaches the ${}^2B_1$ state of AH_2 from the viewpoint of potential energy surface and is of importance for heavy AH_3 molecules because of the rather strong spin-orbit coupling.

5. Primary Process in Photochemical Decomposition of AH_2 Molecules

The photolysis of the AH_2 molecules, such as H_2O, H_2S, etc., has been investigated by several authors. The first absorption of H_2O and H_2S occurs as a continuum below 1780 Å and 2600Å, respectively[4,5]. The primary process of photochemical decomposition in this absorption has been considered as follows:

$$AH_2 + h\nu \longrightarrow AH + H.$$

Electronic Structure.—The AH_2 molecule is an isosceles triangle with symmetry C_{2v}. The electron configuration of the ground state ${}^1A_1$ is $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^2$, and that of the first excited states ${}^{1,3}B_1$ is $K(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)(3a_1)$. The $1a_1$ and $1b_2$ orbitals are strong-bonding, while the $2a_1$ is weak-bonding and its bonding power increases with decreasing bond angle of ∠HAH′. The highest occupied orbital $1b_1$ is non-bonding and the lowest vacant orbital $3a_1$ is also nearly non-bonding and has $(n+1)s$-like property of the A atom. The vacant orbital ra_1 is strong-antibonding and its antibonding power increases with decreasing bond angle of ∠HAH′[21] and also with increasing ordinal number of Periodic Group of the central atom A, because of the increase of p-character[25].

On the other hand, the AH radical is a linear form with symmetry $C_{\infty v}$. The electron configuration of the ground state ${}^2\Pi$ is $K(1\sigma)^2(2\sigma)^2(1\pi)^3$, in which the 1σ orbital is strong-bonding and the 2σ orbital is weak-bonding while the 1π orbital is non-bonding. The excited states of the AH radical also exist, for example ${}^2\Sigma^+$ $K(1\sigma)^2(2\sigma)(1\pi)^4$ and ${}^2\Sigma^+$, ${}^{2,4}\Sigma^-$ and ${}^2\Delta$ $K(1\sigma)^2(2\sigma)^2(1\pi)^2(3\sigma)$, but they are rather high as compared with the first excited states of the corresponding AH_2 molecule. Accordingly, they are not responsible for this reaction and are not discussed here in detail.

TABLE IV

CORRELATIONS BETWEEN REPRESENTATIONS OF GROUPS $C_{2v}-C_s-C_{\infty v}$ AND $C_{2v}-D_{\infty h}-C_{\infty v}$

C_{2v}	C_s	$C_{\infty v}$
A_1, B_2	A'	Σ^+, Π, Δ,……
A_2, B_1	A''	Σ^-, Π, Δ,……

C_{2v}	$D_{\infty h}$	$C_{\infty v}$
A_1	Σ_g^+, Π_u, Δ_g,……	Σ^+, Π, Δ,……
A_2	Σ_u^-, Π_g, Δ_u,……	Σ^-, Π, Δ,……
B_1	Σ_g^-, Π_u, Δ_g,……	Σ^-, Π, Δ,……
B_2	Σ_u^+, Π_g, Δ_u,……	Σ^+, Π, Δ,……

Potential Energy Surface.—The AH_2 molecule with symmetry C_{2v} (or $D_{\infty h}$) dissociates to AH+H passing through the intermediate with symmetry C_s (or $C_{\infty v}$). Then, Table IV gives the correlations between representations of groups $C_{2v}-C_s-C_{\infty v}$ and $C_{2v}-D_{\infty h}-C_{\infty v}$. The ground state ${}^1A_1$, the first excited states ${}^{1,3}B_1$ and the repulsive excited states ${}^{1,3}B_1$ of the AH_2 with symmetry C_{2v} correspond to respectively the ground state ${}^1A'$, the first excited states ${}^{1,3}A''$ and the repulsive excited

---

[23] D. A. Ramsay, *J. Chem. Phys.*, **25**, 188 (1956).

[24] In this case, the ${}^{ev1,3}A_1$ state, or the ${}^{ev1,3}E$ states, which correlate with the first excited states ${}^{1,3}A_1$, correlates with the ${}^{ev1,3}A'$ states, or the ${}^{ev1,3}A'$ and ${}^{ev1,3}A''$ states, of the intermediate AH_3 molecule with symmetry C_s. Accordingly, all the species come into question and therefore the vibronic correlation rule is not especially important to determine this primary process.

[25] This is the result of the increase of the ionization energy difference between the ns and the np orbital of the A atom.

states $^{1,3}A''$ of the AH_2 with symmetry C_s. By increasing one of the AH internuclear distances, the first excited states $^{1,3}B_1$ reach the $^{2,4}\Pi$ states $K(1\sigma)^2(2\sigma)(1\pi)^3(3\sigma)$ of the AH radical and the 1s ^2S state of the H atom in the approximation of single configuration, while the ground state $^1A_1$ and the repulsive excited states $^{1,3}B_1$ reach the ground state $^2\Pi$ $K(1\sigma)^2(2\sigma)^2(1\pi)^3$ of the AH radical and the 1s ^2S state of the H atom. Accordingly, the crossings between the first and the repulsive excited states take place. But the ra_1 orbital is very strong-antibonding, so that the antibonding property of the first excited states due to the interaction between the $3a_1$ and the ra_1 orbital is not so weak, and the elevation of the potential energy curves of these states to the crossing points may be small. As the result of this, the actual potential energy curves may not have a maximum point as shown in Fig. 4, and the first absorption spectrum of the molecule appears as continuous (case (2b) of the rule in Chapter 2)[26]. It is noted that such an argument is generally valid when the linear first excited states are realized.

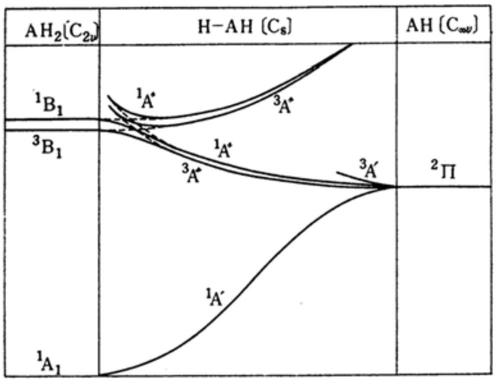

Fig. 4. Potential energy curves for photochemical decomposition of AH_2 molecule. The relative energy scale of the right and the left part was chosen to fit the H_2O molecule and the OH radical.

Primary Process.—In the AH_2 molecule, the influence of vibration is not so important, because all the decomposition to the $^2\Pi$ state of AH are electronically allowed[27]. Accordingly, the primary process in the photochemical decomposition of the AH_2 molecule can be explained as follows: the AH_2 molecule absorbs a rather short wave-length (for example, about 1800 Å for H_2O and about 2600 Å for H_2S) and is excited to the first excited state $^1B_1$[17]. The excited molecule dissociates to the $^2\Pi$ state of the free AH radical and the 1s ^2S state of the H atom due to some of the AH stretching vibration, passing through the intermediate with symmetry C_s. In this case, the realization of the linear intermediate with symmetry $C_{\infty v}$ may also be possible, since the equilibrium bond angle ∠HAH′ in the first excited states may be expected to be fairly large as compared with the ground state. Meanwhile, the electronic property of the highest singly occupied orbital changes from $(n+1)s$-like non-bonding to strong-antibonding beyond the above-mentioned crossing. The process passing through the singlet-triplet transition can also be considered, but the products are the same as in the above case and the possibility may be small from the viewpoint of spin conservation. The conclusion in the present discussion is consistent with the experimental result that the fluorescence of the OH radical has never been observed in the direct photolysis of the H_2O molecule[28].

6. Some Remarks

The discussions in the present paper are rather similar to those of Mulliken[29] and of Walsh[7,8]. The purpose of these papers, however, was the explanation of spectra of the AH_N molecules and others and not of the primary process in photochemical decomposition, so that the discussion of potential energy surface were hardly done at all. Moreover, in the former, the available data at that time were rather few so that the discussion are not necessarily complete at present. In the latter, the $(n+1)s$-like orbital ϕ_5 and the antibonding orbital ϕ_r were separately treated, so that the explanations are not only ambiguous but involve some error. Accordingly, the present paper may be said to be the first one relevant to the primary process in photochemical decomposition in the approximation of the molecular orbital.

---

[26] The difference of the potential energy surface between the cases of diffuse and continuous bands may be expected to be small by taking into consideration of the results of the free CH_3 and CD_3 radcials (G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956)).

[27] The AH_2 molecule with symmetry C_{2v} has three fundamental vibrations: two with species a_1 and one with species b_2. For the first and repulsive excited states $^{1,3}B_1$, therefore, the corresponding vibronic states are $^{1,3}B_1 \times A_1 = {}^{ev1,3}B_1$ and $^{1,3}B_1 \times B_2 = {}^{ev1,3}A_2$. As can be seen from Table IV, they evidently correlate to the $^2\Pi$ state of the AH radical, since the AH has only one stretching vibration σ.

[28] L. O. Brown and N. Miller, *Trans. Faraday Soc.*, **51**, 1623 (1955).

[29] R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

In the present consideration, the vacant orbitals were treated as nearly non-bonding $(n+1)s$-like and strong-antibonding. In the precise discussion, however, this consideration is not always sufficient to the present purpose, and the mixing of the $(n+1)s$ and higher orbitals, or more strictly the effect of configuration interaction, must explicitly be included. In that case, the crossing between the potential energy curves with the same symmetry and the same spin multiplicity need not be taken into consideration and more satisfactory results will be expected. For example, the potential energy curve of the first excited singlet state of NH_3 will be obtained so as to give an explanation of the predissociation without the crossing. However, it may be said that the present consideration based on the approximation of single configuration is also convenient to a schematic understanding of the reactions.

The author wishes to thank Professor S. Shida for his helpful advice and kind discussion. He also wishes to thank Mr. Y. Mori for his valuable suggestion and instructive discussion. This research is supported in part by the grant in aid for the miscellaneous scientific researches of the Ministry of Education.

Laboratory of Physical Chemistry
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo