Electronic Structures of Polyatomic Molecules. VII. Ammonia and Water Type Molecules and Their Derivatives

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Spectroscopic and ionization potential data are used in obtaining electron configurations in terms of molecular orbitals for NH_3, PH_3, H_2O, H_2S and their derivatives, e.g., CH_3NH_2, $(CH_3)_2NH$, N_2H_4, H_2O_2, CH_3OH, NH_2Cl, $ClOH$, Cl_2O. These electron configurations hold for molecules in their normal states, but can be used in predicting the energy of "vertically" excited states, i.e., energies corresponding to nuclear dimensions the same as for the normal state. Frequent close similarities between the spectra of parent molecules and their derivatives are explained (also the similarities between alkyl halides such as CH_3I, C_2H_5I, etc.). Estimates of vertical ionization potentials for the various orbitals used are given. Various points (types of orbitals used, Rydberg series, predissociation) are touched on. The longest wavelength ultraviolet spectra and minimum ionization potential are attributed in the NH_3 derivatives to excitation of a nearly nonbonding electron of the N atom, in the H_2O and H_2S derivatives to excitation of a nonbonding O or S atom electron. (Exception: compounds containing I, Br, and perhaps Cl, where the halogen atom supplies the most easily excited and ionized electron.)

I. AMMONIA DERIVATIVES

IN a recent paper,[1] conclusions concerning electronic structures and their relations to ultraviolet spectra and ionization potentials were summarized for certain methane derivatives, particularly those of the CH_3X type (X = halogen). A similar summary is given here for derivatives of NH_3, H_2O, and of analogous molecules such as PH_3, H_2S. The structures are expressed in terms of electron configurations, using atomic orbitals for unshared electron configurations, molecular orbitals of various types for shared electrons.[2, 3]

The normal state of NH_3 (pyramidal form, symmetry C_{3v}), omitting the N atom $1s$ electrons, may be described[2] as:

$$[sa_1]^2[\pi e]^4[za_1]^2, \ ^1A_1, \quad (1)$$

Appr. loc.   N $NH_?$ N
Vert. I   (27)   (16)   11.

Symbols a_1, e, and A_1 are systematic classification symbols,[1, 2] appropriate to symmetry C_{3v}. Symbols s, π, z are particular symbols briefly descriptive of the orbital in question. The orbital

$[sa_1]$ is primarily an N atom $2s$ orbital, shared a little by all three H atoms,[2] and so contributes a little to all three N−H bonds. The pair of orbitals $[\pi e]$ is degenerate; they have forms which might in rough approximation be built up from N atom $2p\pi$ (i.e., $2p_x$ and $2p_y$) combined with H atom $1s$ orbitals; they give strong N−H bonding. The main bonding characteristics and approximate locations of the various orbitals are summarized under the configuration (1).

The orbital $[za_1]$ is roughly just a $2p\sigma$ (i.e., $2p_z$) *nonbonding* orbital of the N atom. The pure $2p_z$ form (z axis = axis of symmetry of NH_3) is, however, somewhat modified in a way which can be roughly described as by admixture of $2s_N$ and of $1s$ of the three H's, and contributes a little to the three N−H bonds. The observed ionization potential I (11.1 volts) of the NH_3 molecule can safely be identified as the I (= term value) of $[za_1]$. This value may be compared with the value 12.2 volts approximately predicted for the vertical I of a nonbonding $2p_z$ by methods described in an earlier paper.[3] (This prediction supersedes one[2] made by less adequate methods.) The agreement is as good as is found in other cases.[1, 3] Part of the discrepancy may be accounted for by a lack of complete verticality in the observed I. ("Vertical" or Franck-Condon I corresponds to ionization without change in molecular dimensions; "adiabatic" I, i.e., minimum I allowing readjustment of molecule to new equilibrium, is necessarily less, although the difference should be very small for I of a com-

[1] R. S. Mulliken, Phys. Rev. **47**, 413 (1935). Strongly supported by results of W. C. Price, Phys. Rev. **47**, 419, 510 (1935).

[2] *a.* Cf. R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933) and earlier papers. *b.* Also J. Chem. Phys. **3**, 375 (1935), in regard to the general nature of the method (VI of this series). Also in VIII, XI, XII of this series, there are given further details as to the forms of the molecular orbitals indicated here by brief symbols.

[3] R. S. Mulliken, Phys. Rev. **46**, 549 (1934); J. Chem. Phys. **2**, 782 (1934): cf. especially Table IV.

pletely nonbonding electron.) Under the electron configuration (1) are also given estimated vertical I's (semi-empirical method of reference 3) for other orbitals.

Since $[za_1]$ has by far the lowest I (I_{min}) of the orbitals which are occupied in the normal state of NH_3, its excitation should be responsible for the longest wavelength ultraviolet bands. As has been noted before,[1, 2] the frequency at which ultraviolet absorption begins should run approximately parallel to I_{min}.

If we regard the lower excited states of NH_3 as built by adding an electron in an excited orbital to an NH_3^+ core

$$[sa_1]^2[\pi e]^4[za_1], \, ^2A_1 \qquad (2)$$

corresponding to removal of one $[za_1]$ electron from configuration (1), then if we can predict the nature and energies of the possible excited orbitals, we can predict the excited states. It seems probable[2] that all excited orbitals here are nearly like atomic orbitals, forming Rydberg series: $3s$, $4s$, $5s$, $\cdots$ (all of type a_1), $3p\pi$, $4p\pi$, $\cdots$ (type e), $3p\sigma$, $4p\sigma$, $\cdots$ (type a_1), $3d\delta$, $4d\delta$, $\cdots$ (type e), $3d\pi$, $4d\pi$, $\cdots$ (type e), $3d\sigma$, $4d\sigma$, $\cdots$ (type a_1), etc. It may be, however, that some of these series, or at least their lowest members, will show abnormalities because of their relationships to orbitals in the core (cf. the abnormal $y\sigma$ orbitals of He_2).

If the excited orbitals are sufficiently atom-like, $3sa_1$ should be the lowest, giving configuration (3) for the lowest excited states :[2]

$$[sa_1]^2[\pi e]^4[za_1](3sa_1), \, ^3A_1, \, ^1A_1. \qquad (3)$$

The observed ultraviolet absorption bands starting near $\lambda2200$ have been attributed already[2] to a transition from (1) to the $^1A_1$ state of (3). Transitions to the $^3A_1$ should be much weaker and displaced probably slightly toward longer wavelengths. The vertical term value of $3sa_1$ can be found approximately by subtracting the excitation potential for the intensity maximum[4a] (about $\lambda1900$) of the $(1)\rightarrow(3)^1A_1$ transition from I of $[za_1]$. The result is about 4.6 volts, a reasonable term value for $3s$ here. Recent work[3a] on the $(1)\rightarrow(3)$ bands of ND_3 should be mentioned. This indicates that the state (3) and therefore probably the normal state (2) of NH_3^+ has a

[3a] W. S. Benedict, Phys. Rev. **47**, 641A (1935).

plane equilibrium form. This is in harmony with suggestions made previously.[2] The absorption observed beginning near $\lambda2300$ in PH_3, AsH_3, SbH_3 (wholly continuous in all, except for two diffuse bands $\lambda\lambda2315$, 2290 in PH_3)[4] doubtless involves excitation of $[nza_1]$ to $(n+1)sa_1$ just as in NH_3.

In regard to (3), it may be noted that the NH_3^+ core *per se* should be stable, since the electron removed is essentially nonbonding. This does not, however, avert the possibility of predissociation of excited NH_3, which may be thought of as due to interaction of the excited electron with the core in such a way that the former becomes split off together with a hydrogen nucleus of the latter: $NH_3'^+\epsilon\rightarrow NH_2+H$. According to this viewpoint, predissociation should tend to diminish with increase in the principal quantum number of the excited electron. Data on NH_3 and observed Rydberg series in other molecules seem to be in general agreement with this expectation.[4a]

We are now in a position to give a simple explicit reason for the striking similarity which has been observed between the ultraviolet absorption spectra of NH_3 and several of its derivatives, namely, hydrazine (N_2H_4) and several amines (CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$).[5] In all of these, absorption begins about $\lambda2300-2500$ with a series of more or less diffuse bands and increases in intensity and diffuseness toward the ultraviolet; and the total intensity is about the same in all. It seems strongly improbable that these resemblances are merely superficial or fortuitous, although one should always bear the possibility in mind. The similarity between NH_3, CH_3NH_2, etc., has been explained by Herzberg and Kölsch[5] by saying that excitation is localized in the NH_2 group.

We can now be more specific and attribute the observed absorption in all the foregoing cases to excitation of a nearly nonbonding $[z]$ electron belonging essentially to the N atom,

[4] G. H. Cheesman and H. J. Eméleus, J. London Chem. Soc. 2847 (1932).

[4a] A. B. F. Duncan, Phys. Rev. **47**, 822 (1935): vacuum ultraviolet NH_3 spectrum.

[5] G. Herzberg and R. Kölsch, Zeits. f. Elektrochem. No. 7b (1933): amines, etc.; also unpublished photographs of W. C. Price on CH_3NH_2. S. Imanishi, Nature **127**, 782 (1931): hydrazine. Recently, V. Henri and W. Lasareff, Compt. rend. **200**, 829 (1935): methylamine.

and going in each case to a $3s$ excited orbital centered around (although not really belonging exclusively to) the N atom. Thus the excitation is localized around and characteristic of, not the NH_2 group, but rather the trivalent N atom.

This explanation implies that the orbitals $[z]$ and $(3s)$ persist without essential change when H atoms of NH_3 are replaced by substituents $(CH_3$, etc.), in spite of changes in symmetry. This is entirely reasonable, as we shall see, provided the angles between the three bonds going out from the N atom, and the mean distribution of electricity surrounding the N atom, remain nearly constant. Conversely, from the constancy of the spectrum we have strong support for the constancy of these features of the bonds. An analogous explanation can be applied to the fact[5a] that $P(C_2H_5)_3$ shows absorption in nearly the same region as PH_3.

The structures of the NH_3 derivatives can best be understood by considering first the effect on an NH_3 molecule of a slight displacement of one H atom in such a way as to reduce the symmetry from C_{3v} to C_s. The symmetry group C_s possesses as elements only the identity operation and reflection in a single plane of symmetry through the N and one H atom. Such a distortion splits up any degenerate orbital (type e) of C_{3v}. In this way, $[\pi e]$ of (1) and (2) splits into two orbitals which may be called $[xa'']$ and $[ya']$, where the yz plane passes through the nonequivalent H atom (cf. reference 2, Fig. 1a; also reference 2, Eqs. (2) for approximate forms of $[x]$, $[y]$). Representations a' and a'' are respectively symmetrical and antisymmetrical relative to the plane of symmetry. We then

have for NH_3 with symmetry C_s:

$$[sa']^2[xa'']^2[ya']^2[za']^2, {}^1A'. \qquad (4)$$
$$\text{N} \quad NH_2 \quad NH \quad \text{N}$$

The letters under the orbitals indicate approximately the localization or function of the orbitals, e.g., $[x]$ gives bonding between N and two of the H atoms, $[y]$ between N and the third (the displaced one); $[s]$ and $[z]$ are, roughly, nonbonding N atom orbitals, although more precisely they give some bonding to all three H's, almost equally to all.

Electron configurations can now be written for various derivatives of NH_3. In NH_2X, for example (X = halogen), X is substituted for the displaced H, and $[y]$ takes on the burden of the $N-X$ bond, while $[x]$ remains practically unchanged; $[s]$ and $[z]$ are nearly unchanged, except that they participate slightly in the $N-X$ and the two $N-H$ bonds, instead of in three $N-H$ bonds as in NH_3. In considering the spectrum of NH_2X, the nonbonding $np\pi_X$ electrons may be of importance, just as in CH_3X,[1] because of their low I values. The case is, however, somewhat different from CH_3X in that here the central atom N is able to furnish an electron $[za']$ of I low enough to compete with I of $np\pi_X$. Study of the I data for $np\pi_X$ in CH_3X indicates, however, that I_{min} in NH_2X also is probably I of an $np\pi_X$, except in NH_2F and possibly NH_2Cl. The next lowest I is then that of $[z]$ of the N atom.

For CH_3NH_2 a good electron configuration can easily be written down from a comparison of those of CH_3X and of XNH_2. The result is:

$$CH_3NH_2 \text{ (symm. } C_s); \; [sa']^2[sa']^2[xa'']^2[xa'']^2[ya']^2[ya']^2[za']^2, {}^1A' \qquad (5)$$

approx. location	N	CH_3	NH_2	CH_2	CH	NC	N
est. I	(27)	(22)	16	14.5	13.5	11.	

Formulation (5) applies to the probable equilibrium arrangement of the atoms, with $C-N-H$ and $H-N-H$ bond angles similar to the $H-N-H$ angles in NH_3. Free rotations around the $C-N$ bond will, of course, upset this and

will spoil the rigorous symmetry C_s, leaving, however, an approximate local symmetry C_{3v} within the CH_3 group and C_s within the NH_2. Nevertheless this does not really mean any serious alteration in the orbitals given in (5), but only some changes in their technical classifications.

In (5) we really have, essentially, the orbitals

[5a] H. W. Thompson and J. J. Frewing, Nature **135**, 507 (1935): ethyl and methyl derivatives of NH_3, PH_3, H_2O, H_2S; etc.

$[sa_1]$ and $[\pi e]$ of the CH_3 radical (C_{3v}), but technically, for the equilibrium arrangement, $[\pi e]$ is slightly split up into $[xa'']$ and $[ya']$ in accordance with the total symmetry C_s. These orbitals $[\pi e]$ are nevertheless expected to be practically the same as in CH_4 or in CH_3X, and should have nearly the same I as in those molecules (cf. discussion of $[\pi e]$ in CH_3X in reference 1). Similarly, we have $[xa'']$ of NH_2 and $[za']$ of N nearly the same as in NH_3 or NH_2X, and $[sa']$ not far different than in NH_2X or NH_3. Finally we have $[ya']$ which in LCAO approximation[7b] is of the form $[(2p_v)_N + 2p\sigma_C]$. This links the C and N and is intermediate in character between the $C-C$ bonding orbital $[\sigma + \sigma, a_1]$ of C_2H_6 (symm. D_3, similar to C_{3v}, see IX of this series) and the $N-N$ bonding orbital $[y]$ of N_2H_4 (see Eq. (6) below), of LCAO form $(2p_y + 2p_y)$.

Strictly speaking, the orbitals of CH_3NH_2 cannot be quite so much localized as (5) would indicate. There is necessarily some interaction and mixing between all indicated orbitals of type a', and again between all those of type a''. In particular, the orbitals $[sa']_{NH_2}$ and $[sa']_{CH_3}$ must both participate somewhat in the $C-N$ bond, as one sees for instance by noting that $[s]$ in CH_4 participates in all four bonds, $[s]$ in NH_3 in all three bonds. Nevertheless (5) represents about the best simple system of orbitals that one can assign, and in the writer's opinion probably corresponds fairly well to the true situation. The similarity of the CH_3NH_2 to the NH_3 longest wavelength ultraviolet absorption is rather satisfactory empirical evidence that orbital $[za']_N$ is nearly the same in CH_3NH_2 as in NH_3, in spite of the fact that some mixing with other orbitals of type a' must exist. In particular, one would not have been surprised to find strong mixing between $[za']_N$ and $[ya']_{NC}$, hence a pronounced change in forms of the orbitals with the changed symmetry. The spectroscopic evidence that this effect is not important gives us considerable assurance that other possible mixings among the approximate orbitals indicated in (5) can also tentatively be neglected. The existence of free rotation (if it is a fact here) also indicates lack of strong interactions between $[\pi e]$ of CH_3 and the orbitals of NH_2. Other evidence indicating lack of interaction between

such nearly non-overlapping orbitals of different radicals will be cited in VIII of this series.

The foregoing discussion indicates that in setting up electron configurations for complex molecules, one can often with some assurance assume close resemblance between orbitals of derivative and parent molecules, even when rigorous symmetry considerations fail one. (Most derivatives are relatively complex and lacking in rigorous symmetry.) This principle must, however, be used with caution. It cannot be expected to apply in extreme cases where bond angles or bond strengths depart markedly from those of the parent molecules.

In connection with the foregoing principle, it is found that, even though we start with the idea of using nonlocalized orbitals, approximate localization often occurs automatically, e.g., $[z]$ in NH_3 derivatives apparently remains approximately localized as in NH_3 in spite of opportunities for mixing with other orbitals to form nonlocalized resultants. In our discussion of CH_4 and NH_3 derivatives (reference 1 and here) we have arrived quite naturally at electron configurations containing not only highly localized (atomic) orbitals, but also two kinds of semi-localized orbitals: (1) "*radical*," i.e., intra-radical, orbitals, e.g. $[s]$ of CH_3 and NH_2, $[\pi]$ of CH_3, $[x]$ of NH_2; and (2) inter-radical orbitals, e.g., $[y]$ of the $C-N$ bond in CH_3NH_2 or of the $N-X$ bond in XNH_2. Radical orbitals are nonlocalized with respect to a radical but localized so far as the molecule as a whole is concerned. In some cases, as $[\pi]$ of CH_3 in CH_3NH_2 or CH_3X, this localization is largely automatic; in others, e.g. $[s]$ of CH_3 or NH_2, which tend to mix with the inter-radical bonding orbital, we impose localization in part arbitrarily for the sake of simplicity, in the same way that we use atomic orbitals for electrons of two atoms in a molecule when such orbitals can be so chosen as not to interact very much. As for inter-radical orbitals, which usually giving inter-radical bonding in the case of normal states, these often tend automatically to be largely localized in the region of the bond, although this is by no means always the case.

Returning now to CH_3NH_2, we notice that in order that this may give an absorption spectrum closely resembling that of NH_3, it is necessary

not only that $[za']$ in (5) shall be nearly the same as in NH_3 but also that the excited orbital $3s$ shall be nearly the same in both. [Conceivably, of course, both $[za']$ and $3s$ could be different than in NH_3, yet give a very similar spectrum, but this is improbable.] It is important to note that the orbital $3s$ is so large (estimated effective radius about 2.6×10^{-8} cm) as partly to overlap the CH_3 group ($N-H$ and $C-H$ distances each about 10^{-8} cm, $C-N$ distance about 1.5×10^{-8} cm). Hence it cannot be considered as localized on the N atom. Nevertheless, since the excited electron $[za']$ has come out of the N atom, the center of attraction for the $3s$ is located near the N nucleus, both in NH_3 and in CH_3NH_2 and likewise in $(CH_3)_2N$, $C_2H_5NH_2$, and other amines. This is probably sufficient to permit the needed close similarity of the excited orbital in all these cases.

Following the line of approach indicated above, it is possible to write reasonable electron configurations for $(CH_3)_2NH$, $(CH_3)_3N$ and others. In doing so, complications arise because of variations in symmetry and for other reasons. Some of the complications, such as changes in technical classification of orbitals depending on symmetry, small splittings-up of orbitals which in cases of high symmetry (as e.g. in parent molecules) are degenerate, are more apparent than real. In other words, conspicuous changes in rigorous technical designations of orbitals often correspond to relatively trivial changes in actual forms of orbitals. This is illustrated in the difference between (1) and (4).

As another example of NH_3 derivatives, we may consider the hydrazine molecule (N_2H_4). The molecule as a whole is probably totally lacking in symmetry,[6] so that no classification of orbitals is possible as regards symmetry type. The normal state, omitting inner $1s$ N atom electrons, may be described as

$[s]^2 \; [s]^2 \; [x]^2 \; [x]^2 \; [y]^2 \; [z]^2 \; [z]^2, {}^1A$ (6)
$N_A \; N_B \; N_AH_2 \; N_BH_2 \; N_AN_B \; N_A \; N_B$
$27 \; \; 27 \; \; \; 16 \; \; \; \; 16 \; \; \; \; 15 \; \; \; 11 \; \; 11$

N_A and N_B refer to the two N atoms. More or less mixing must occur between the orbitals indicated. In particular, resonance must occur

between the members of each pair of like-designated orbitals, e.g., $[z]_A$, $[z]_B$, so that each such pair must be represented by a pair of I values. Approximately, however, these resonance and other effects, and the resulting splitting up or other changes of I values, may probably be neglected, in the same way that we neglect the resonance between, e.g., the $1s$ nitrogen non-bonding atomic orbitals which are tacitly part of (6).

The similarity of the N_2H_4 to the NH_3 spectrum is then accounted for, provided $3s$ is nearly as in NH_3. Actually, resonance between $3s_A$ and $3s_B$ can surely not be neglected, since these would overlap very strongly. Instead of $3s_A$ and $3s_B$ we must then have two new forms roughly like $a(3s_A+3s_B)$ and $a'(3s_A-3s_B)$. However, one finds that the former of these will be not very different from a $3s$ orbital centered about a point half-way between the two N nuclei and so is probably nearly enough like $3s$ of NH_3 to fill our need.

II. DERIVATIVES OF WATER AND HYDROGEN SULPHIDE

The electron configuration for the normal state of H_2O (symmetry C_{2v}, z axis = symmetry axis, x axis = perpendicular to HOH plane) can be written, omitting inner-shell electrons, as follows:[1]

$$(2sa_1)^2[yb_2]^2 \; [za_1]^2(2xb_1)^2, {}^1A_1 \quad (7)$$
$approx. \; location$ O   HOH   HOH   O
$I_{vert} =$ (32)   (18)·   (17)   12.7

The orbitals $2s$ and $2x$ (i.e., $2p_x$) are essentially nonbonding O atom orbitals, while $[y]$ and $[z]$ both participate in both $O-H$ bonds. Estimated vertical I's are given below. The value 12.7 volts for $2x$, however, is an observed value from electron impact data.[7] Another value of 12.9 volts is obtained from the edge of a strong continuous absorption in the far ultraviolet,[8] which probably represents approximately the convergence point of Rydberg series involving excitation of $2x$. Absorption continua[8] with fairly well marked long wavelength edges at 16.7 ± 0.5 and 17.8 ± 0.5 volts may similarly

[6] Cf. W. G. Penney and G. B. B. M. Sutherland, J. Chem. Phys. 2, 492 (1934).

[7] H. D. Smyth and D. W. Mueller, Phys. Rev. 43, 116 (1933).

[8] G. Rathenau, Zeits. f. Physik 87, 32 (1933).

correspond to the estimated I's for $[y]$ and $[z]$. The I observed at about 16 volts by electron impact[7] doubtless also corresponds to $[y]$ or $[z]$ or both. In this connection it should be recalled that the observed minimum I's obtained from Rydberg series or their limiting continua are adiabatic I's and should always be smaller than estimated vertical I's in the case of bonding electrons (e.g., $[y]$, $[z]$). In the case of electron impact I's and adiabatic I's, values varying between vertical I's and adiabatic I's may perhaps be obtained depending on the delicacy of detection.

The observed minimum I of H_2O of about 13 volts, attributed to the nonbonding $(2xb_1)$, may be compared with the value 14.7 volts approximately predicted for a nonbonding $2p_x$ of oxygen by the methods earlier described.[3] As in the case of the nonbonding orbitals $[za_1]$ of NH_3 and $(np\pi_1)$, etc., of CH_3I, etc., the observed value is somewhat less than the predicted.

As lowest excited states of H_2O one might expect

$$(2sa_1)^2[yb_2]^2[za_1]^2(2xa_1)(3sa_1),\ ^{3,\ 1}A_1. \quad (8)$$

The observed continuum starting rather sharply at 6.9 volts ($\lambda1780$) and having its maximum at about 7.5 volts may be reasonably attributed to transitions to the $^1A_1$ of (8), with much fainter transitions to the $^3A_1$. This interpretation gives a reasonable vertical term value ($I=$ about $12.7-7.5=5.2$ volts) for $3s$. The fact that the transition gives continuous absorption must be attributed to predissociation, apparently into $O(p^4,\ ^1D)+H_2(^1\Sigma^+_g)$.[9, 12]

The molecule H_2S should have normal and lowest excited configurations analogous to (7) and (8), but with quantum numbers one greater $(3sa_1,\ 3xb_1,\ 4sa_1,$ etc.) and with smaller I's. The observed minimum I of H_2S (10.4 volts according to electron impact data[10] and about 10.42 volts from Rydberg series found by Price[11]) undoubtedly is a nearly vertical I corresponds to removal of a $(3xb_1)$ nonbonding electron. Al-

though Price reports two very slightly different Rydberg series limits, it is clear that there can be only one insofar as electronic energy is concerned.

The molecules H_2S, H_2Se, H_2Te all show absorption continua[12] attributable to a transition $(nx)\rightarrow(n+1)s$ like the first ultraviolet continuum of H_2O. These continua are displaced toward longer wavelengths with increasing molecular weight (first absorption maximum at about 7.5, 6.2, 5.9 volts for H_2O, H_2S, H_2Se). The position of the maximum, combined with I, gives for H_2S a reasonable vertical term value for the excited orbital $4sa_1$. The value is $10.4-6.2=4.2$ volts, compared with 5.2 for $3s$ in H_2O.

Just as the longer wavelength ultraviolet spectra of NH_3 derivatives resemble closely those of NH_3, so we might expect similar resemblances between H_2S and H_2O derivatives and the respective parent molecules. Likewise the minimum I of such derivatives would be expected, provided complications (e.g., atoms like I or Br containing nonbonding electrons of lower I) are absent, to be that of the nonbonding (x) orbital and roughly the same as in the parent molecule. Price[11] predicts that I will decrease somewhat as alkyl groups are substituted for H atoms in H_2S or H_2O. Available spectroscopic data[5a, 11, 13, 16, 19] tend to support the foregoing expectations.

Electron configurations of H_2O derivatives can be set up, as in the case of CH_4 and NH_3 derivatives, by starting from a distorted H_2O molecule, here a symmetry C_s, obtained by displacing one H atom slightly. This gives instead of (7),

$$(2sa')^2[ya']^2[za']^2(xa'')^2,\ ^1A'. \quad (9)$$

Orbitals $[y]$ and $[z]$ now belong to the same representation and can mix. Since they are probably of nearly equal energy in H_2O or H_2S (cf. XII of this series), they may mix rather strongly if the distortion is made large, or if one H is replaced by another atom or radical making the strengths of the two bonds decidedly different. Mixing between $[y]$ and $[z]$ is equivalent to a rotation of axes. The extreme of mixing

[9] M. Kimura, Sci. Papers Inst. Phys. Chem. Res. **18**, 150 (1932).

[10] C. A. MacKay, Phys. Rev. **24**, 319 (1924).

[11] W. C. Price, J. Chem. Phys. **3**, 256 (1935); Bull. Am. Phys. Soc. **10**, 9 (1935). The writer is greatly indebted to Dr. Price for an opportunity to see these in manuscript form, as well as for other unpublished data.

[12] C. F. Goodeve and N. O. Stein, Trans. Faraday Soc. **27**, 359–572 (1931).

[13] H. Ley and B. Arends, Zeits. f. physik. Chemie **B15**, 311 (1932): H_2S and its alkyl derivatives.

would be represented by two new orbitals $[y'a']$, $[z'a']$ with axes y', z' directed (for a 90° bond angle) along the two bonds, and differing by 45° from the axes of $[y]$ and $[z]$. The nonbonding orbital (xa''), belonging to a different representation a'' (antisymmetrical to the symmetry plane) is not affected by any such mixing or rotation of $[y]$ and $[z]$.

A molecule like ClOH would be represented by (9), plus nonbonding electrons of Cl, particularly the group $(3p\pi)_{Cl}^4$, whose I should be near and probably less than that of (xa''). Spectra of HOCl and HOBr in water solutions are known.[14] The absorption is continuous, beginning near $\lambda 3300$ and increasing fairly steadily. The HOBr absorption curve is displaced about 0.4 volt toward longer wavelengths as compared with HOCl.

Cl_2O (symmetry C_{2v} like H_2O) should be represented by (7) plus two sets of $(3p\pi)_{Cl}^4$. The fact that Cl_2O shows continuous absorption throughout the visible and ultraviolet[15] (with maxima near $\lambda\lambda6300$ (weak), 5800 (weak), 4300, and 2500 (strong) seems, however, difficult to reconcile with such an electron configuration. The longer wavelength absorption has been shown to produce dissociation into $O+ClO$.[15]

The apparent discrepancy with our expectations may perhaps be reconciled somewhat as follows: (1) It should be clearly noted that our theory considers primarily only *vertical* processes of ionization and excitation (molecular dimensions constant). (2) Although an absorption maximum is usually a guarantee of vertical excitation (hence our continual use of the energies of absorption maxima, not of long wavelength edges), this may not always be true for weak maxima, such as those at $\lambda\lambda6300$, 5800, 4300. It may be that these maxima represent vertical excitation with respect to certain coordinates, e.g., the $Cl-O$ distances, but not with respect to all, e.g., perhaps not for the $Cl-O-Cl$ angle. (3) For a linear (or otherwise altered) $Cl-O-Cl$ it is perfectly possible that the electron configuration and I values would be greatly altered as compared with (7). Hence if

the weak maxima represent transitions which are partially oblique (i.e., nonvertical, or anti-Franck-Condon) it is in principle quite possible to account for the necessary low energy excited electron states. (4) As a side-light it is worth noting that in some sense, or in some degree, it is impossible to draw a sharp line in polyatomic molecules between nonvertical processes with continuous absorption, and predissociation processes.

The foregoing discussion is important in showing that our present approach needs to be greatly extended (by a study of electron configurations and vertical I values for every conceivable configuration of nuclei) in order to permit a complete account of the electronic states and spectra of polyatomic molecules. Nevertheless the present approach should represent a good beginning, especially when nonbonding electrons are excited to high (Rydberg) levels, or are ionized.

For CH_3OH (symmetry C_s, or none, with $C-O-H$ bond angle presumably nearly like the $H-O-H$ angle in H_2O) we might have

$$(2s)^2[s]^2\ [z']^2[y']^2[\pi]^{2+2}(2x)^2,\ ^1A \quad (10)$$

approx.

location O CH₃ OH OC CH₃ O
est. I 32 22 17.5 16 14.5 12.5

Here $[s]$ and $[\pi]$, the latter here really split into two orbitals differing slightly in energy, belong essentially to CH_3, $(2s)$ and $(2x)$ to O, while $[z']$ and $[y']$ together give the $O-H$ and $O-C$ bonding. Formula (10) is written corresponding to the extreme y', z' orientation of axes, localizing the $O-H$ bonding in $[z']$ and the $C-H$ bonding in $[y']$. The actual orbitals must, however, be mixtures of these extreme forms, although very likely the mixing may not be strong. At any rate, $(2x)$ should probably be practically free from mixing and should have the lowest I. Ultraviolet absorption of CH_3OH begins near $\lambda 2000$, and is continuous, with the first maximum at about 6.9 volts (cf. H_2O, 7.5 volts).[16] C_2H_5OH shows a very similar absorption.[16] It is reasonable to suppose that this absorption has the same explanation (transition

[14] K. Schaefer, Zeits. f. physik. Chemie **93**, 312 (1919).
[15] Cf. Goodeve and Wallace; and W. Finkelnburg, H. J. Schumacher and G. Stieger, Zeits. f. physik. Chemie **B15**, 127 (1931).

[16] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).

$2x \rightarrow$ probably $3s$) in CH_3OH and C_2H_5OH as in H_2O. A similar statement applies to the quite similar continua of $(CH_3)_2O$ and $(C_2H_5)_2O$ with maxima at about 6.5 volts.[16, 11] Similar relations hold between the absorption spectra of H_2S, C_2H_5SH, $(CH_3)_2S$, etc.[13] The situation resembles that for NH_3, CH_3NH_2, $C_2H_5NH_2$, $(CH_3)_2NH$, etc., although there the presence of discrete bands makes the argument more certain.

For NH_2OH one might now expect:

NH_2OH (*no symm.*):

$$(2s)^2[s]^2[z']^2[y']^2(2x)^2(z)^2, {}^1A, \quad (11)$$

O   N OH ON O   N
32 27 17.5 17 13 11.5

modified by more or less mixing between $[z']$ and $[y']$. NH_2OH is reported to be transparent even in concentrated solutions at least to about $\lambda2200$.[17] This is reasonably in harmony with our expectations.

For H_2O_2,[6] we may write:

H_2O_2 (*no symm.*):

$$(2s)^2(2s)^2[y']^2[z']^2[z']^2(2x)^2(2x)^2, {}^1A, \quad (12)$$

O   O OO OH OH O   O
32 18   17.5   13

modified by more or less mixing and resonance between the approximate orbitals indicated. The observed absorption spectrum of H_2O_2 is a continuous one increasing steadily in intensity from $\lambda3750$ (2.3 volts) to at least $\lambda2150$ (5.75 volts) and producing dissociation into two OH both in their normal state ${}^2\Pi$ at the longer, and into one ${}^2\Pi$ and one excited ${}^2\Sigma^+$ at the shorter wavelengths.[18] The long-drawn-out absorption extending to long wavelengths may be due to nonvertical excitation processes (cf. discussion of Cl_2O). Since the first maximum of absorption evidently comes below $\lambda2150$, and may come near that of H_2O, it is quite possible that for vertical excitation, the lowest energy excitation process is $2x \rightarrow 3s$ as in H_2O. (Of course $3s$ here must be centered between the two O atoms, not around one; cf. discussion of N_2H_4 above.)

Another possibility which should be considered is that $3s$ is not the lowest vertically excited orbital here. The O–O bonding orbital $[y']$ in (12) is really of the LCAO form $(2p_{y'} + 2p_{y'})$,

and there should be a corresponding excited orbital $(2p_{y'} - 2p_{y'})$ which may be fairly low in energy here: cf. the analogous orbitals $(np\sigma + np\sigma, \sigma_g)$ and $(np\sigma - np\sigma, \sigma_u)$ which are, respectively, the bonding and the lowest excited orbital in the halogen molecules X_2.[3] Possibly the longer wavelength absorption in H_2O_2 is due to a weak transition $(2x) \rightarrow (2p_{y'} - 2p_{y'})$. A similar possibility may be involved in ClOH and other cases (even Cl_2O).

Something analogous also would also seem possible in N_2H_4, NH_2Cl, NH_2OH. The N–N bonding orbital $[y]$ in N_2H_4 in (6) is of LCAO form $[p_y + p_y]$, like $[y']$ of H_2O_2 in (12), and there should be an excited orbital $[p_y - p_y]$ which might be of low energy. The spectra, however, do not indicate the existence of any excited orbital of lower energy than would be reasonable for $3s$. It must be admitted that our conclusions as to low excited orbitals are in many cases still very tentative. The normal state configurations are much more certain.

III. Alkyl Halides

In conclusion, it is of interest to return, in the light of the foregoing discussion, to certain molecules mentioned in a previous article.[1] It is found that there is an extraordinary similarity between the ultraviolet absorption spectra of all alkyl iodides (CH_3I, C_2H_5I, C_3H_7I, etc.) down to $\lambda1500$ at least.[16, 11, 20] Each has a continuum near $\lambda2600$ (upper level A) and a pair of band systems, closely similar to each other, near $\lambda1900$ (upper levels B and C). The systems involving B and C differ in the heavier alkyl iodides as compared with CH_3I mainly just in having a more complex fine structure. This is presumably due to a small splitting-up of degenerate orbitals by reduction in symmetry, or to added vibrational degrees of freedom, or both. Also in some of the heavier iodides the bands are more diffuse and the C component lacking, very likely because of predissociation.

The close similarities among the various alkyl iodide spectra remind one of those noted above among the various alkylamine spectra (CH_3NH_2,

[17] Baly and Desch, J. London Chem. Soc. **93**, 1747 (1908).
[18] H. C. Urey, L. H. Dawsey and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

[19] G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933); R. A. Rehman, R. Samuel and Sarf-ud-Din, Ind. J. Phys. **8**, 537 (1934).
[20] W. C. Price, J. Chem. Phys. **3**, 365 (1935): ethyl halides, with their I's.

$C_2H_5NH_2$, etc.) and between CH_3OH and C_2H_5OH, and they probably have a similar explanation. It has been shown[1] that the A, B and C levels of CH_3I all result from excitation of a nonbonding $5p\pi$ I atom electron out of a closed group $5p\pi^4$, the energy interval $C-B$ agreeing with that to be expected for $^2\Pi_{\frac{1}{2}} - ^2\Pi_{1\frac{1}{2}}$ of the group $5p\pi^3$ of I. The same explanation is applicable to the other alkyl iodides (C_2H_5I, etc.).

In order to account for the almost identical position, in all these iodides, of the spectra leading to these excited levels, it is necessary that the excited orbitals involved should be nearly the same in all (cf. our discussion of the NH_3 derivatives). It would be plausible to suppose that, since the excitation takes place in the I atom leaving the latter as a positively charged center, the excited orbital also is local-
ized around this atom. The simplest assumption would be that in the A level the excited orbital is $6s$ of iodine, in the B and C levels it is another iodine orbital, perhaps $6d\pi$. (Certain features of the CH_3I bands make it probable that the excited orbital is of the e type (to which $6d\pi$ belong) in the B, C, levels.) Both these orbitals would be large and would overlap the neighboring atoms but should not be much altered by the change from CH_3I to C_2H_5I, etc. In the previous article,[1] other suggestions as to the excited orbitals were made, according to which they were ascribed to the region of the $C-I$ bond or of the CH_3 group in CH_3I. It is probably best to leave the question of the exact nature of the excited orbitals open for the present, except that on the basis of the spectra it seems clear that they are localized *near* the I atom.

Electronic Structures of Polyatomic Molecules. VIII. Ionization Potentials

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Observed and predicted values for ionization potentials of nonbonding electrons are compared, and the differences attributed mainly to charge-transfer effects. Multiplet interval and other criteria are cited as evidence that assumed nonbonding orbitals are really such, i.e., that they are effectively localized and interact little with other orbitals. The prediction of ionization potentials for bonding and antibonding electrons is also discussed. The present paper grows, in part, from suggestions of Price as to the effects of dipole fields on ionization potentials.

I. Nonbonding Orbitals

IN pursuing a program[1, 2, 3, 4] of describing molecular electronic structures in terms of electron configurations, it is of considerable importance to be able to make approximate predictions as to the ionization potentials (I) corresponding to various types of orbitals in molecules. Methods for doing this were outlined in previous papers.[5] Since a considerable body of empirical data has now accumulated on observed I's, it appears desirable at this point to see what conclusions can be drawn from a comparison between these and predicted I's. This will make possible a refinement of our I predictions, and will be found important in helping us reach definite conclusions as to electron configurations.

We shall first consider orbitals which are essentially nonbonding, since for these the predicted I's (of the type I^*)[5] are much more

[1] R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935): VI of this series.
[2] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933): V.
[3] R. S. Mulliken, Phys. Rev. **47**, 413 (1935).
[4] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935): VII.
[5] R. S. Mulliken, Phys. Rev. **46**, 551 (1934); J. Chem. Phys. **2**, 789–793 (1934). See also J. Savard, J. de phys. et rad. [VII] **4**, 650; **5**, 27 (1934), and elsewhere.

* In examining Table I, one should bear in mind that the predicted I values for Br and I are somewhat uncertain because of lack of complete spectroscopic data on the atoms; also that observed I values obtained by electron impact methods (unstarred in the table) are likely to be appreciably in error; and finally that the observed I values may