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$\text{C}_2\text{H}_5\text{NH}_2$, etc.) and between CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, and they probably have a similar explanation. It has been shown¹ 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 ${}^2\Pi_4$ – ${}^2\Pi_1$ of the group $5p\pi^3$ of I. The same explanation is applicable to the other alkyl iodides ($\text{C}_2\text{H}_5\text{I}$, 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 $\text{C}_2\text{H}_5\text{I}$, 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**)⁶ 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

TABLE I. Observed and predicted I 's for nonbonding electrons.

ATOM	ELECTRON IONIZED TYPE	PRED. I		OBSERVED I FOR			
			A_2	H_nA	CH_3A	C_2H_5A	
I	$5p\pi$	10.85	10.0	12.75	9.49†	9.30†	
Br	$4p\pi$	12.28	12.8	13.25	10.49†	10.24†	
Cl	$3p\pi$	13.62	13.2	13.75, 12.9	11.17†	10.8†	
S	$3p_z$	10.83		10.42†			
O	$2p_z$	14.73		12.7			
N	$2p_z$	12.24		11.1			

Notes. Predicted I 's are I^* 's obtained by method of Ref. 5; in the case of sulfur, data from J. Ruedy, Phys. Rev. **44**, 757 (1933) are used. Observed I 's are from electron impact methods, except those marked with a dagger; these are from Rydberg series limits of spectra by W. C. Price (Phys. Rev. **47**, 419, 510 (1935) and Bull. Am. Phys. Soc. **10**, 9 (1935). In the case of halogen compounds, the predicted and observed I 's refer to the lower ($^2\Pi_{1/2}$) of the two values corresponding to the states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ of the positive ion (or analogous states in the polyatomic cases). Added in proof: the value 12.9 ± 0.2 for HCl is from A. O. Nier and E. E. Hanson, Bull. Am. Phys. Soc. **10**, 10 (1935). The values for C_2H_5X are from W. C. Price, J. Chem. Phys. **3**, 365 (1935).

definite than for bonding or antibonding orbitals, and have a better theoretical foundation. Available data on observed and predicted I 's for such orbitals are given in Table I.

Although the data in Table I are few, certain trends are evident. In analyzing these,* one should first note that the I predictions are directly applicable only to cases in which the orbital of the ionized electron is (a) perfectly nonbonding and at the same time (b) in an environment (charge distribution) the same as for a free atom. More or less departure from these ideal conditions is to be expected in practise. Interactions of the given orbital with those in other atoms may result in bonding or antibonding tendencies and so cause deviations from (a), while changes in the force field due to molecule-formation, including the accumulation of net positive or negative charges on atoms, may cause deviations from (b). Besides deviations from (a) and (b), departures from a "normal" relation, in respect to electron distribution, between the molecule and its positive ion might conceivably be important, but probably are not so in practise. Some discussion bearing on this point will appear in XI of this series.

If we consider the quantities ($I_{pred} - I_{obs}$) from Table I it will be noticed that for each type H_nA or CH_3X , $I_{pred} - I_{obs}$ increases (or becomes decreasingly negative) as we go to more electronegative A or X atoms. (The

probable order of increasing electronegativity⁶ is H, I, S, C, Br, Cl, N, O.) This effect is just what we might expect, since the accumulation of negative charge on an electronegative atom (e.g. O in H_2O) should make I_{obs} less than I_{pred} .⁵ The effect is not observed in the homopolar molecules X_2 , where there is no net transfer of charge.

We have, however, not yet accounted for everything. For example, $I_{pred} - I_{obs} = +1.36$ volts for CH_3I , although C and I are nearly equal in electronegativity according to Pauling.⁶ Consideration of the fact that the C in CH_3 must bear a considerable net negative charge and the H's a corresponding positive charge solves the difficulty, however. Price has suggested⁷ that the resulting field of the CH_3 dipole $H_3^+C^-$ accounts partly for the low I_{obs} in CH_3I (and in CH_3Br , CH_3Cl , and other cases). At the same time the C in CH_3 should share its excess negative charge with the I, thus lowering I_{obs} more directly. It is rather artificial to attempt to separate dipole and direct charge accumulation effects, and it is convenient to lump them together under the heading of charge-transfer effects.

While charge-transfer accounts well for $I_{pred} - I_{obs}$ in most cases, it evidently does not suffice for the type HX . In HI, $I_{pred} - I_{obs} = -1.9$ volts, while from charge-transfer one would have expected a small positive value. The observed I 's in HCl, HBr, HI may be explained if we assume that, superposed on the normal charge-transfer effect, there is another effect increasing I by about 1.5–2 volts. It is not clear what can be the source of so large an effect, however. Possibilities that occur to one, although they appear quantitatively inadequate, are: united-atom tendency (penetration of H^+ within outer shell of I atom electrons, enough to out-balance effect of the negative electron it brings with it); taking on of some bonding power by $5p\pi$, by interaction with the excited orbital $2p\pi$ of hydrogen. It seems hardly worth while to pursue the matter further. Possibly the I_{obs} data, based on electron impact, are seriously in error, although they appear to be unusually

be slightly low because of lack of complete verticality. These doubtful factors, however, are in the aggregate probably not of serious importance, and will be tentatively neglected here.

⁶ L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

⁷ W. C. Price, Phys. Rev. **47**, 444, 510; J. Chem. Phys. **3**, 256, 365 (1935).

reliable. *Added in proof:* a new electron-impact value for HCl is indeed somewhat lower than the old, while Price (private communication) gets some evidence of Rydberg series leading to lower I 's than the old electron-impact values.

In the cases of H_2O , NH_3 and H_2S , it may be noted, the values of $I_{\text{pred}} - I_{\text{obs}}$ agree very well with what one might expect on the basis of charge-transfer. There is no indication of effects like those in HX, although the possible causes suggested above for the behavior of HX should still operate.

We have not yet considered (except for HX) the possibility that some of the $I_{\text{pred}} - I_{\text{obs}}$ deviations may be a result of departure from the ideal nonbonding condition, due to interaction with other orbitals. Such interactions must of necessity exist; it is a question here of their importance. The effect should be greatest in cases like Cl_2 , where a group $(3p\pi)^4$ is present in each atom. Resonance between the two localized $3p\pi$ atomic types tends to replace them by two new molecular types, one bonding $(\pi + \pi, \pi_u)$ and one antibonding $(\pi - \pi, \pi_g)$.⁵ The latter should have the smaller I , which should therefore correspond to I_{obs} ; and if the resonance effect is strong, I_{obs} might for this reason be considerably smaller than I_{pred} . The values of I_{obs} for Cl_2 , Br_2 and I_2 , although probably not very reliable, tend to indicate that this resonance effect is small, hence that the use of the nonbonding atomic orbitals is a good approximation.

Similar interactions, but smaller because of lack of exact resonance, are to be expected e.g. between the two nonbonding types $3p\pi_{\text{Cl}}$ and $5p\pi_{\text{I}}$ in ICl ⁶ and between the CH_3 radical type $[\pi e]$ and the I atom type $5p\pi_{\text{I}}$ in CH_3I .³ In the case of each interacting pair, $5p\pi_{\text{I}}$ has the smaller I . Interaction would tend to give a bonding orbital $(a\pi_{\text{Cl}} + b\pi_{\text{I}})$ or $(a[\pi]_{\text{CH}_3} + b\pi_{\text{I}})$ and an antibonding orbital $(a'\pi_{\text{I}} - b'\pi_{\text{Cl}})$ or $(a'\pi_{\text{I}} - b'[\pi]_{\text{CH}_3})$, where $a > b$, $a' > b'$, I being increased for the bonding, decreased for the antibonding orbital. For $a=1$, $b=0$, we have the ideal nonbonding case. Since the $I_{\text{min}} = I_{\text{obs}}$ of ICl and CH_3I is attributed to $5p\pi_{\text{I}}$, any interaction should tend to decrease I_{obs} . I data are lacking for ICl , but for CH_3I (and CH_3X) we might be inclined to attribute the negative

values of $I_{\text{obs}} - I_{\text{pred}}$ (of Table I) largely to such interactions, rather than just to charge-transfer.

Fortunately, there is definite evidence whereby these questions can be settled. The answer is that the interactions are not strong. To begin with, the evidence of the I data on X_2 , cited above, should be recalled. Further evidence is found in the fact that the ultraviolet spectra,⁵ Rydberg series in particular,^{7, 8} involving excitation of one of the nonbonding electrons, show very little vibrational structure. This means that the bonding is little affected by high excitation or removal of the electron in question. This could hardly be true if strong interactions existed between the assumed nonbonding groups of electrons, since the latter would then be replaced by strongly bonding and antibonding groups.

Finally, the intervals $\Delta\nu(^2\Pi_1 - ^2\Pi_{11})$ observed in the spectra of ICl , IBr , BrCl , and of CH_3Br and CH_3I ,⁵ and particularly the $\Delta\nu$'s of CH_3I^+ , CH_3Br^+ , and CH_3Cl^+ obtained from Rydberg series by Price,⁸ give rather conclusive independent evidence that the interactions mentioned must be small (i.e., b , b' small) in these molecules, so that they may reasonably be neglected.

The evidence from the $\Delta\nu$'s is as follows. Taking ICl as an example, if one had $(a'\pi_{\text{I}} - b'\pi_{\text{Cl}})$ with a' and b' nearly equal, the observed $\Delta\nu$ should be about half-way between those of the Cl and I atoms. Similarly in CH_3I , it should be half-way between $\Delta\nu$ of CH_3 (about zero) and $\Delta\nu$ of I. If, however, $a'=1$, $b'=0$, $\Delta\nu$ should agree approximately with that of the I atom.^{9, 3} In all cases the observed $\Delta\nu$'s are found to be in harmony with $a'=1$. Strictly speaking, however, the predicted $\Delta\nu$ should be somewhat increased or decreased according as the I atom has a net positive or negative charge,⁹ e.g., $\Delta\nu$ for I should be about 0.69 volt on the basis of I^+ , 0.625 volt on the basis of neutral I; observed in CH_3I^+ is 0.62 volt. Presumably the net charge is strongly positive in the excited or ionized states for which the $\Delta\nu$'s are observed. Hence the $\Delta\nu$'s tend to indicate that a' is not quite 1, but nevertheless that $a'=1$, $b'=0$ is much more nearly right than $a'=b'$.

⁵ W. C. Price, Phys. Rev. **47**, 419, 510 (1935).

⁹ Ref. 5, p. 559.

Summarizing, we conclude that the deviations $I_{pred} - I_{obs}$ for nonbonding atomic orbitals are mainly due to charge-transfer (except in $HX^?$), and that the use of such localized nonbonding atomic orbitals gives good approximations; also that intraradical-bonding orbitals such as $[\pi e]$ of CH_3 may safely be considered as localized, i.e., treated as radical orbitals which are nonbonding so far as interactions with other orbitals are concerned. This last conclusion is in harmony with other evidence in regard to relations between parent molecules and their derivatives.⁴

II. BONDING AND ANTIBONDING ORBITALS

It is obvious that charge-transfer effects should be important not only for the I 's of nonbonding orbitals, but also for those of bonding and antibonding orbitals. Price⁷ has already emphasized the importance of dipole effects in this connection. The semi-empirical rules previously set up⁵ may be stated as follows:

$$I_{pred} \geq \frac{1}{2}(I_A^\circ + I_B^\circ), \quad (1)$$

where the upper inequality sign refers to bonding, the lower to antibonding orbitals, and the I 's are calculated as earlier indicated.⁵ A and B refer to the two atoms forming the bond; if the orbital is a nonlocalized one involving several atoms, the necessary generalization of (1) is easily made. If atoms A and B have effective net charges, the I 's and I_{pred} must be altered accordingly, but probably not more than 1 or 2 volts in most cases for neutral molecules. Just how large such corrections should be may perhaps best be determined by experience. The same applies to the magnitude of the inequalities

indicated by (1); in practice these appear usually to be of the order of 1-3 volts.

For a heteropolar bond involving the usual electron-pair (i.e., excluding the case of one-electron bonds), the charge-transfer effect will generally tend to make I_A° and I_B° more nearly equal than they are for the free atoms. This is because the more electronegative atom usually has the larger I° , which should then usually be decreased by charge-transfer, while the smaller I° , belonging to the more electropositive atom, is at the same time increased. For a homopolar bond, I_A° and I_B° will both be increased or decreased together by charge-transfer, if any. Here the transfer is to or from A and B , from or to other atoms in the molecule. (Example: C-C bonding orbital in C_2H_6 , where I° 's should be decreased due to $H_3^+C^-$ polarities. This may be expressed, following Price,⁷ by saying that I should be decreased by the effects of the two C- H_3^+ dipoles.)

In XI of this series it will be shown that the use of molecular orbitals logically implies a comparison not with I° 's of atoms which (at least for the average of A and B) are neutral, but with much smaller I° 's, call them N° 's, corresponding to a condition (cf. Hund) about half-way between neutral atom and negative ion. Instead of (1), this would yield the condition $I_{pred} \gg \frac{1}{2}(N_A^\circ + N_B^\circ)$ for bonding and perhaps $I_{pred} > \frac{1}{2}(N_A^\circ + N_B^\circ)$ for antibonding orbitals. Such relations, however, are probably unfruitful, since the N 's are not accurately known and the magnitudes of the inequalities are large. In practice, the as yet essentially empirical relations (1) promise to be much more useful, since experience so far has shown them reliable.

Electronic Structures of Polyatomic Molecules. IX. Methane, Ethane, Ethylene, Acetylene

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Electron configurations for the normal states of C_2H_4 , C_2H_6 , and C_2H_2 are given, and are used in interpreting observed ionization potentials. Excited orbitals of CH_4 and the others are also discussed and tentative interpretations given for the ultraviolet spectra. "Reduced" interatomic distances are studied as a measure of overlapping and resonance of orbitals of different atoms or radicals.