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Discontinuous Change of Binding Type in the Series of Monohydrides.* III. Regularities and Irregularities of Internuclear Distances and Force Constants

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The recently attempted correlation of internuclear distances of the monohydrides of all elements by linear plots of $\log r$ vs $\log Z$ (atomic number) for each of the two octaves and of the three long periods is not satisfactory. The equations $r_e = 2.2240 n^{-0.426}$ and $r_0 = 2.7793 n^{-0.371}$ (n is the total number of valence electrons in the hydride) apply merely from HF to BH and from HCl to AlH, respectively. The marked deviations from these equations shown by the hydrides M(I)H and M(II)H are related to a discontinuous change of binding type. In the long periods, r increases for the hydrides of the heavy metals from M(I)H to M(III)H, due to the decrease of polarizability and penetrability of the cations with an 18-electron ($s^2 p^6 d^{10}$) outer shell, e.g., from AgH to InH. It is emphasized that the knowledge of spectroscopic data for molecule ions of the hydrides of long period elements is necessary in order to decide at which places discontinuous changes of binding type occur.

1. EMPIRICAL CORRELATIONS

THE plot of internuclear distances (r) in the series of monohydrides LiH to HF and NaH to HCl against the numbers of the groups of the periodic system I to VII show (Fig. 1, Segmented Lines I and II) in general a systematic decrease of the slopes of the consecutive segments. However, the slopes of the segments BC and AlSi are irregular, being larger instead of smaller, than those of the segments BeB and MgAl, respectively.^{1,2} This was expressed numerically (Comment I) by deriving the quotients Q' between the r values of adjacent members of the series. In general they decrease within each series, e.g., from 1.0904₅ for NaH/MgH to 1.0518 for HS/HCl, however AlH/HSi = 1.0830₅ is larger than *both* adjacent Q' .

During a valuable correspondence concerning the question, in which way this irregularity is connected with the assumed discontinuous change of quantization from $\bar{e}_{n-1}M^{n+}H^-$ to $(H^+, X^{(n+1)+})\bar{e}_{n+2}$, M. A. Bredig, in July 1964, brought to my attention that the place at which the irregularity occurs in the first octave can be made graphically especially evident when one plots

$\log r$ or $1/r$ vs $\log n$: the part of the line after boron is very nearly linear.

Independently, Blinder showed me recently a preprint of a note³ which contains the proposal of a linear representation of $\log r_e$ vs $\log Z$ (atomic number of the element forming the hydride) not only for the *whole* first and second octave but also for the long periods KH to HBr, RbH to HI, and CsH to BiH. This cannot be brought into agreement either with the above-mentioned irregularities in the first two octaves or with the statement in I (based on Refs. 1 and 2): "in the series CuH to HBr, AgH to HI, and AuH to BiH, the gradation of properties from the first to the third group is different from that for hydrides of the light metals." The following comments, made with the knowledge of Bredig and Blinder, appear, therefore, justifiable.

In order to find out which selection of abscissa and ordinate gives the best linear plot within the first two octaves, the following combinations of coordinates have been tried: for the ordinate $\log r$ or $1/r$, for the abscissa the log either of Z or of the number of the group of the periodic system or of the total number n of valence electrons of the hydride, i.e., $\log 2$ for LiH and NaH, $\log 8$ for HF and HCl. The latter choice combined with $\log r$ proved to be the most favorable.

* K. Fajans, J. Chem. Phys. **40**, 1773 (1964) (I); **41**, 4005 (1964) (II).

¹ K. Fajans and T. Berlin, see Refs. 3 and 4 in I.

² K. Fajans, "Chemical Binding Forces," Shell Development Company Emeryville, California; Technical Report No. 57-59, 1953.

³ C. E. Jentelson and S. M. Blinder, J. Chem. Phys. **42**, 4306 (1965).

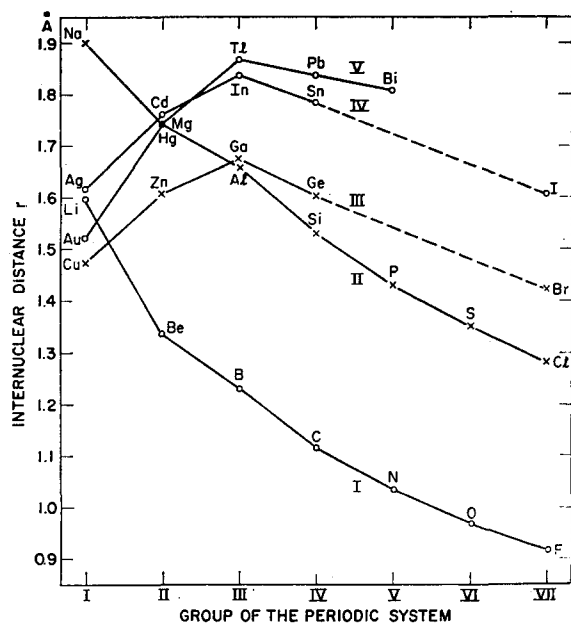


FIG. 1. Internuclear distances of monohydrides vs the group numbers of the periodic system of the element combined with hydrogen. The circles (O) designate r_e values. Since they are not known for HP, HS, and GaH, the distances in Series II and III are given as r_0 and designated by crosses (X). The r_e of HgH (1.7404) is so close to r_0 of MgH (1.7431) that they are represented by a single filled circled (●).

In Fig. 2, Line I shows from F to B hardly any, Line II from Cl to Al only a very slight systematic deviation from linearity. However, the slopes of the BeB and MgAl segments are, respectively, 1.42 and 2.14 times smaller than those of the adjoining straight lines. The slopes of the LiBe or NaMg segments are, respectively, nearly equal or 1.74 times smaller than those of the corresponding straight lines. Therefore the construction of least-squares straight lines (I and II in Ref. 3) for the whole octaves, obscures the most significant aspect of the interrelations involved.

The situation for the monohydrides of the members of the long periods is still more complex. The $\log r$ vs $\log Z$ plots (III, IV, and V in Ref. 3) show considerable irregular deviations of the experimentally precise points from the drawn least-squares lines. This has the following reasons.

The segmented lines, III, IV, V in Fig. 1, have in common with the lines I, II the decrease of r between the III and VII group (V for Bi). However, pronounced maxima occur for GaH, InH, TlH, because from Group I to Group III the values of r increase in the lines III, IV, V, contrary to their decrease in the lines I and II. The incomplete parts to the right of the maxima would show larger deviations from linearity, if plotted logarithmically. In any case the representation³ of the r values for the three long periods by equations of the type $r = aZ^{-b}$ is not satisfactory because b has opposite signs on the two sides of the maximum. However, the

equations $r_e = 2.2240n^{-0.426}$ and $r_0 = 2.7793n^{-0.371}$ apply from BH to HF and from AlH to HCl, respectively.

2. RELATION WITH ELECTRONIC STRUCTURE

2.1. Cations of Noble-Gas Type

The empirical correlations, discussed above, interest us mainly in connection with the discontinuous change of the binding type assumed to occur in these series. Initially¹ the sign of the change of binding strength (B.S.) on ionization was considered as the most reliable criterion of the binding type in the neutral molecule, and it was concluded that, e.g., in the first octave the discontinuous change takes place after BH. This was supported and specified in I and II on the basis of the change of B.S. on excitation and by comparison of the energetic stabilities of the structure BH and HB: it was concluded that the discontinuous change occurs between BH and HC. On the other hand, MO considerations led Blinder⁴ to the view that the place is between BeH and HB.

The irregular gradation of the slopes of the segments around B and Al, shown in Fig. 1 and somewhat more clearly in Fig. 2, supports further the view that such discontinuity exists. The attempt to decide, on the basis of these irregularities alone, the place of the discontinuous change in these two octaves leads to the following result.

Starting with Li in Fig. 1, one would expect that if the hydrides of B and C had the same type of structure as have LiH and BeH, the segment BC should be less steep than BeB. The fact that the opposite is true can mean that while BH is the correct formulation, r for

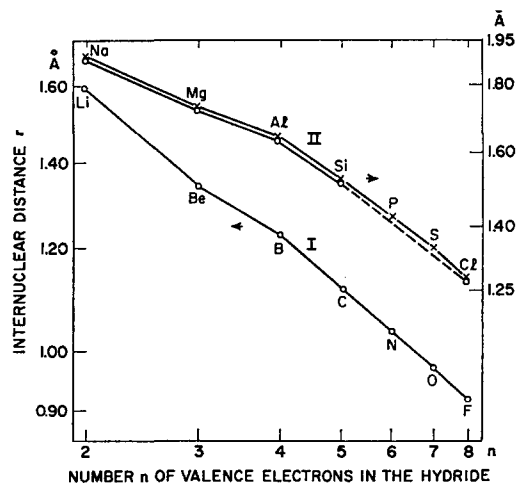


FIG. 2. Plot of $\log r$ vs $\log n$, the total number of valence electrons in the molecule, i.e., 2 for LiH and NaH, 8 for HF and HCl. The distinction between the circles and crosses is the same as in Fig. 1. The scale on the left ordinate applies to the Series I, that on the right ordinate to the Series II.

⁴ S. M. Blinder, J. Chem. Phys. **41**, 4004 (1964).

TABLE I. Internuclear distances (r in angstroms) and force constants (k in millidynes per angstrom) in neutral and ionized, ground and excited states of CdH.

	CdH	(CdH)*	(CdH)*	(CdH) ⁺	(CdH) ⁺⁺
State	$X, {}^2\Sigma^+$	$A, {}^2\pi$	$B, {}^2\Sigma$	$X, {}^1\Sigma^+$	$A, {}^1\Sigma^+$
r_e	1.761 ₇	1.663 ₃	[2.39] ^a	1.667 ₂	1.865
k_e	1.2043	1.8185	[0.5804]	1.8545	0.9222
Q.F.	$\bar{\epsilon}\text{Cd}^{2+}\text{H}^-$	$\bar{\epsilon}^*\text{Cd}^{2+}\text{H}^-$	$\bar{\epsilon}\text{Cd}^{2+}(\text{H}^-)^*$	Cd^{2+}H^-	$\text{Cd}^{2+}(\text{H}^-)^*$

^a The values in brackets for the B state apply to r_e and k_e .

the hydride of C is shorter, i.e., this molecule is more stable than the structure CH. Accordingly, the discontinuous change would take place between BH and HC.

However, as Bredig pointed out, starting in Fig. 2 with HF, the regularity of the line FB seems to indicate that the hydride of B has still the structure HB. The r value for the hydride of Be is smaller than expected for the continuation of the straight line, hence the discontinuous change seems to take place between BeH and HB. This inconsistency shows that, whereas the irregularity of the slopes indicates that the discontinuous change of the structure takes place around B (the same applies to Al and to the consideration of force constants^{1,2}) it does not in itself allow one to decide whether this change occurs to the left or to the right of the III group.

2.2. Cations of Nonnoble-Gas Type

The spectacular difference between the series I, II, and III, IV, V, in Fig. 1, with respect to the gradation of the r values within the first three groups of the periodic system⁵ has been discussed by Berlin (Ref. 4 in I) with the following results. If one formulates all monohydrides involved as $\bar{\epsilon}_{n-1}\text{M}^{n+}\text{H}^-$, the cation M^{n+} has noble-gas type in the series I, II, but an 18-electron ($s^2p^6d^{10}$) shell in III, IV, V; the latter shell is responsible for a more pronounced mutual polarization of the ions M^{n+} and H^- (see the bibliography since 1923 in Footnote 2 of Ref. 5 in I); the polarizability and penetrability of M^{n+} increase from Group III to Group I and the influence of these factors on the B.S. of the hydrides of these heavy metals is more important than that of the increase in the charge of M^{n+} , which is decisive in the first two octaves. The maximum of r for GaH, InH, TlH is due to the competition between these two influences and possibly to the change of quantization from the type $\bar{\epsilon}_{n-1}\text{M}^{n+}\text{H}^-$ to $(\text{H}^+, \text{X}^{(n+1)+})\bar{\epsilon}_{n+2}$ after the group III.

The consideration of the excited states of the monohydrides of these heavy metals makes some of the above conclusions more certain. On the other hand, the place in the series III, IV, V at which the change of quantiza-

⁵ With respect to the long periods, only those parts which start with the subgroup Ib are discussed here. The behavior of the molecules KH, CaH, RbH, etc., is, as far as known, closely analogous to that shown by the Lines I and II.

tion occurs is less definite than it appeared at that time. The main aspects which are presented here briefly are designated in the headings of the following sections.

2.2.1. Q.F. of the Various States of ZnH, CdH, HgH

CdH has been chosen as an example for which, in Table I, numerical data of the internuclear distances r are given in neutral and ionized, ground and excited states. The corresponding force constants k are included for comparison. The source of the data is the same as given in I, Refs. 9 and 10.

The opposite directions of the changes of r and k on excitation as well as on ionization, lead to the unambiguous conclusion that the B.S. increases on excitation to the A state and on ionization of CdH but decreases on excitation to the B state of CdH and to the A state of $(\text{CdH})^+$. These observations and the principles explained in Comments I and II support strongly the quanticule formulations given under Q.F. For instance, the antibinding electron $\bar{\epsilon}$ is excited in the state A of CdH and eliminated on its ionization, but it is H^- which is excited in the B state of CdH and in the A state of $(\text{CdH})^+$.

The only apparent inconsistency among the data of Table I is, that in the case of the transfer from the A state of CdH to the ground state of $(\text{CdH})^+$, the 0.2% increase of r indicates a weakening, while the 2% increase of k implies a strengthening of the binding.

Such inconsistencies occur mainly when *small* changes of r and k are involved. Since ionization is a further step of excitation, this direction of the change of k appears to be a more reliable criterion for judging the sign of the change of B.S. However, this secondary

 TABLE II. Internuclear distance (r in angstroms) in the crystals MF_2 , molecules MH, molecule ions $(\text{MH})^+$.

M	Mg	Zn	Cd	Hg
$[\text{M}^{2+}, \text{F}_2]_n$	1.99 (6) ^a	2.03 (6)	2.333 (8)	2.40 (8)
$\bar{\epsilon}\text{M}^{2+}\text{H}^-$	1.7306	1.5945 ₀	1.761 ₇	1.7404
M^{2+}H^-	1.649	1.514 ₆	1.667 ₂	1.594 ₃

^a The numbers (6) and (8) for the fluorides give the coordination numbers of the cations in the rutile and fluorite structures, respectively. For a precise comparison the r_e values for the latter should be reduced about 2%.

TABLE III. Comparison of the monohydride of Au with those of Cu and Ag, as well as with those of Br and I.

Hydride of	Cu	Ag	Au	Br	Au	I
r_e	1.463 ₁	1.617 ₄	1.5237	1.414	1.5237	1.609
k_e	2.1999	1.8218	3.138	4.1158	3.138	3.1414

question does not need to be decided for the purposes of the present paper.

The data of Table I do not leave any doubt that $\bar{e}\text{Cd}^{2+}\text{H}^-$ and Cd^{2+}H^- are the appropriate Q.F. In a similar way the following closely analogous formulations can be derived: $\bar{e}\text{Zn}^{2+}\text{H}^-$ (State X), $\bar{e}^*\text{Zn}^{2+}\text{H}^-(A)$, $\bar{e}\text{Zn}^{2+}(\text{H}^-)^*(B)$, $\text{Zn}^{2+}\text{H}^-(X)$, $\text{Zn}^{2+}(\text{H}^-)^*(A)$; $\bar{e}\text{Hg}^{2+}\text{H}^-(X)$, $\bar{e}^*\text{Hg}^{2+}\text{H}^-(A)$, $\bar{e}\text{Hg}^{2+}(\text{H}^-)^*(B, C, D)$, $\text{Hg}^{2+}\text{H}^-(X)$, $\text{Hg}^{2+}(\text{H}^-)^*(A)$.

2.2.2. Influence of Polarization on Interionic Binding

As Fig. 1 and Table II show, the internuclear distances in the ground states of these molecules and molecule ions increase in the order Zn, Hg, Cd. The apparently anomalous position of Hg is due to the pronounced role which the mutual polarization of the ions Hg^{2+} and H^- plays in their interaction, because, among its analogs, Hg^{2+} has the largest polarizability, penetrability, and polarizing power.

These effects show up also very clearly when one adds to M^+ or to M^{2+} one electron, instead of H^- . The resulting binding energy (in eV) is numerically identical with the first and second ionization potential of the M atoms. The corresponding values for Hg (10.43, 18.75) are in fact larger not only than those for Cd (8.99, 16.90) but even than those for Zn (9.39, 17.96). Contrary to this, in the crystalline fluorides, in which the multilateral polarization of F^- , much less polarizable than H^- , is of minor importance, the r values in Table II increase in the order Zn, Cd, Hg.

A further demonstration of the significance of the unilateral polarization effects in molecules and ions containing nonnoble-gas-type cations is given in Table II by a comparison with the corresponding magnesium compounds. The value of r for crystalline MgF_2 (1.99) is smaller than that of ZnF_2 (2.03), that for MgH (1.73) is considerably larger than for ZnH (1.59) and very close to that for HgH (1.74), while r for $(\text{MgH})^+$ (1.65) is larger than for $(\text{HgH})^+$ (1.59) in which polarization of H^- is still more pronounced than in HgH .

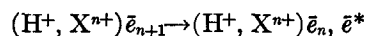
2.2.3. Q. F. of Hydrides of Heavy Metals of Groups other than II

The unambiguous assignment of the quanticule formulations for the hydrides of Group IIb in Sec. 2.2.1

is possible from the knowledge of spectroscopic data for their ionized as well as neutral state and from the fact that for the excited state A of the neutral molecule the B.S. is larger than in the ground state: this proves the presence of an antibinding electron. Contrary to this, no molecule ion has yet been observed for a hydride of any other heavy metal included in Fig. 1 and the B.S. in their known excited states is, with the exception of BiH , smaller than in the ground state. Qualitatively, this is expected for the change



as well as for



and no certain quantitative distinction has been found.

Of the four excited states known for BiH , the state A has a smaller r (1.788 Å) and larger ω (1739.4 cm^{-1}) than the ground state (1.809 and 1698.9, respectively) and B has a still smaller r (1.780), indicating the changes $\bar{e}_4\text{Bi}^{3+}\text{H}^- \rightarrow \bar{e}^*\bar{e}_3\text{Bi}^{3+}\text{H}^-$. If this is correct, then PbH and TIH , rather than HPb and HTI , would be the appropriate formulations, without excluding that the quantization of the monohydrides of Sn and Ge is of the type $(\text{H}^+, X^{4+})\bar{e}_5$. Additional experimental data are necessary in order to decide this question as well as the binding type of the gold monohydride.

It is remarkable that, with respect to the gradation of the r and k values, the hydride of Au exhibits a closer analogy to HBr and HI than to CuH and AgH . As Table III shows, the B.S. of gold hydride is with respect to r smaller, with respect to k much larger than that for CuH . On the other hand, the B.S. of gold hydride is with respect to r intermediate between those of HBr and HI and nearer to the latter, with respect to k it is also smaller than that of HBr and comes very close to that of HI . These interrelations suggest the formulation $(\text{H}^+, \text{Au}^{11+})5^{10}6^2$. Recent considerations⁶ gave for the electron affinity of the Cu atom the value 1.80 eV and one can expect that, due to the pronounced polarizability and penetrability of Au^+ , the electron affinity of Au is still larger. Hence it would not be surprising if the interaction between Au^+ and H^- leads to a discontinuous change towards a binuclear quanticule. If so, the molecule ion $(\text{H}^+, \text{Au}^{11+})5^{10}6^1$ might be observed, as distinct from instable ions such as Na^+H or Ag^+H .

ACKNOWLEDGMENT

I wish to thank Dr. M. A. Bredig for bringing to my attention several relevant points.

⁶ E. Clementi, Phys. Rev. **135**, A980 (1964).