He^{++} ions. The spectroscopic results also indicate that the electrons should have an energy of two to three hundred volts, but higher energy does not seem desirable, especially if accompanied by a decrease of current. Mass-spectrograph experiments are now under way to study the products of ionization under the most satisfactory conditions of operation.

A consideration of other possible sources of He^{++} ions indicates, where calculation is possible, that the percentage of ionization of the gas would be no greater, and probably less in most cases than in the magnetron. The condensed capillary discharge seems to offer one of the best possibilities since the He II lines are very intense relative to those of He I. However, here again, the higher members of the series are relatively less intense than in the magnetron at low pressures, and the concentration of He^{++} ions may be small. Nevertheless, it would be worthwhile to study the products of ionization in the condensed capillary discharge with a mass spectrograph.

In regard to the excitation of ionized spectra in other gases, the magnetron seems to offer some possibilities. The intensity is high close to the filament, and its superiority over ordinary gas discharges was demonstrated strikingly in the case of mercury where many additional lines were brought out by the application of the magnetic field. Whether it can compete with the other devices employed by spectroscopists, such as the electrodeless discharge or the vacuum spark, could probably be determined only with a vacuum spectrograph as most of the strong lines of the highly ionized states lie in the far ultraviolet. It does, however, offer the possibility of intensity studies with electrons of known energy which is not possible with most other sources.

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Low Electronic States of Simple Heteropolar Diatomic Molecules:

III. Hydrogen and Univalent Metal Halides

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Electronic structures for the electronic states involved in the near ultraviolet spectra of AX are discussed (X = halogen, A = hydrogen or univalent metal). The upper electron levels involved are mostly among a set of levels $Q\ {}^1\Pi$ and ${}^3\Pi$, $T\ {}^3\Sigma^+$, $V\ {}^1\Sigma^+$, or their Ω-s or case c equivalents. Tentative potential energy curves for states Q, T and V of HI, AgI, and NaI are shown in Figs. 1–3. It is concluded that the observed HX absorption (continuous) involves the three Q levels corresponding to ${}^3\Pi_1$, ${}^3\Pi_{0^+}$, and ${}^1\Pi$, but with Ω-s coupling. It is further concluded (in contrast to what is found in the halogen spectra) that the observed absorption goes mainly to the ${}^3\Pi_1$ and ${}^1\Pi$ levels rather than the ${}^3\Pi_{0^+}$. The N and V potential energy curves of HX obtained here are compared (see text) with those given by Pauling; for HI there is good agreement, but for HBr, HCl, HF the V curves go increasingly higher than those of Pauling.

For AgX, it is concluded that the upper potential energy curve of the observed bands (curve B) contains a shallow minimum followed, as r is increased, by a maximum, beyond which it sinks to an asymptote about 1 ev lower. It is concluded that curve B is probably a resultant of an interaction of a stable ${}^1\Sigma^+$ curve, derived from a d^9s^2 excited silver atom and an unexcited X atom, with curves of the types $V\ {}^1\Sigma^+$ and especially $Q\ {}^3\Pi_{0^+}$; but that near its minimum state B is essentially $\mathrm{Ag}(d^9s^2)\cdot\mathrm{X}$ in character, corresponding to a stable union between an Ag atom with a d valence electron and an X atom. It is concluded that transitions to the three Q levels in AgX probably involve continuous absorption, as in HX and MX. The various band systems of CuX and AuX at long wave-lengths are ascribed to electron levels derived mainly from metal atoms in which a d electron has been excited (state d^9s^2, ${}^2D$).

For MX (M = alkali metal), it is concluded, in agreement with previous workers, that the process of light-absorption in the near ultraviolet has approximately the effect of transferring an electron from X^- of M^+X^- to the M atom, leaving two neutral atoms M and X which tend to fall apart (case c separate-atom coupling). The thus indicated lack of valence attraction between neutral M and X probably involves a thoroughgoing failure in MX of the additivity rule for homopolar bond energies. Possible reasons for this probable failure (mainly, highly unequal size and energy of valence orbitals of M and X) are discussed. The electronic structures of normal and excited MX (also MX^+) are discussed theoretically both from the molecular orbital viewpoint and from that of atomic orbitals, and the occurrence of case *c* coupling is shown to be theoretically reasonable from both standpoints. The upper levels involved in the absorption are identified as three 1 levels each of which is probably a case *c* mixture of $Q\ {}^3\Pi_1$, $Q\ {}^1\Pi$, and $T({}^3\Sigma^+)_1$, and two 0^+ levels each of which is an approximately 50, 50 mixture of $Q\ {}^3\Pi_{0^+}$ with $V\ {}^1\Sigma^+$.

Franck's empirical spectroscopic criterion for distinguishing between atom-molecules and ion-molecules is discussed. From the present analysis of the electronic states involved in the spectra of HX, AgX, and MX, and from previous work on X_2 and XY, it is concluded that, for molecules containing halogen atoms, the criterion does not have a systematic theoretical basis but, insofar as it is valid, depends on the occurrence of certain rather special and fortuitous circumstances.

1. Introduction

The present paper is a continuation of two recently published,[1, 2] which will be referred to hereafter as "I" and "II." For a general introduction to the present paper, also for certain tables needed in the following, reference should be made to these.

The present paper deals with certain more or less heteropolar diatomic molecule types HX, AgX, and MX containing one halogen (X) atom. The types HX, AgX, and MX, respectively, will be taken up in Sections 5, 6, and 7. Preceding these specific treatments, it appears advisable to make a survey of certain questions which arise and certain rules and principles which are or may be applicable in understanding the spectra and electronic structures of all these molecules. This survey is given in Sections 2–4.

2. Franck's Criterion for Atom- and Ion-Molecules

Franck and collaborators some time ago proposed an empirical spectroscopic criterion for distinguishing between diatomic atom- and ion-molecules (cf. I, Section 4). This proposal has stimulated much interesting work on absorption spectra, particularly of salt vapors. Attempts to extend the criterion to polyatomic molecules, e.g., MeX_2, have not been very successful.

The criterion, considerably qualified subsequent to its original formulation, may be stated as follows:[3] the longest wave-length reasonably strong absorption region involving an electronic transition, in the spectrum of the vapor of the substance in question, corresponds in the case of ion-molecules to dissociation into two unexcited atoms, in the case of atom-molecules to dissociation giving products including at least one excited atom.

The qualifying words "reasonably strong" had to be added when it was found that even atom-molecules in some cases show weak absorption correlated with dissociation into unexcited atoms. Recently the work of Acton, Aickin and Bayliss[4] on Br_2 and of Goodeve and Taylor[13] on HBr and HI make it doubtful whether even the qualification "reasonably strong" is adequate. It now appears probable that the longest wave-length absorption in some or all of the atom-molecules just named is fairly strong yet at the same time gives dissociation into unexcited atoms.

Franck's criterion has hitherto received no theoretical explanation,—except that for atom-molecules like H_2, MH, M_2, where both atoms have a ${}^2S$ normal state, its necessary validity is rather obvious. As already noted, the criterion states that the first region of photodissociation in the case of an ion-molecule yields two unexcited atoms, but that in the case of an atom-molecule it ordinarily leaves one atom in an excited state. Here it deserves emphasis that in practice, for

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[1] R. S. Mulliken, Phys. Rev. **50**, 1017 (1936): I.

[2] R. S. Mulliken, Phys. Rev. **50**, 1028 (1936): II.

[3] *a.* J. Franck, H. Kuhn, and G. Rollefson, Zeits. f. Physik **43**, 155 (1927). *b.* J. Franck and H. Kuhn, Bull. Acad. Sci. United Prov. India **2**, 223 (1933).

[4] R. S. Mulliken, Phys. Rev. **46**, 549 (1934); see also references given there; further, G. E. Gibson and O. K. Rice, Phys. Rev. **50**, 380, 871 (1936); E. Rabinowitch and W. C. Wood, Trans. Faraday Soc., March, 540 (1936); A. P. Acton, R. G. Aickin and N. S. Bayliss, J. Chem. Phys. **4**, 474 (1936); R. S. Mulliken, J. Chem. Phys. **4**, 620 (1936); O. Darbyshire, J. Chem. Phys. **4**, 747 (1936). *Correction:* in the second paragraph on p. 561 of the writer's 1934 paper, next to last sentence, it is stated that "if both were unperturbed, the former [for Ω-*s* coupling] should be about twice as intense as the latter." This is unjustified; no definite relation can be predicted without detailed knowledge of perturbing states. Furthermore, if the high intensity of ${}^3\Pi_{0^+u}\leftarrow{}^1\Sigma^+{}_g$ is the result of a strong perturbation of the ${}^3\Pi_{0^+u}$ state, this is probably due much more to a strong case *c* tendency than to Ω-*s* coupling. *Notes:* In the papers of Rabinowitch and Wood and of Gibson and Rice, support is given to the absorption coefficients and resulting electric moment *P* for I_2 given by the writer in Table II*B* of the 1934 paper. In the other 1936 papers, it is shown that the transition ${}^1\Pi\leftarrow{}^1\Sigma^+$ shares strongly with ${}^3\Pi_{0^+}\leftarrow{}^1\Sigma^+$ and probably ${}^3\Pi_1\leftarrow{}^1\Sigma^+$ in the intensity of the observed Br_2 continuum.

most of the molecules to which the criterion has been applied, the excited state involved has been the $^2P_{1/2}$ upper component of the ground level ^2P of a halogen atom, the excitation thus consisting solely in the occurrence of the $^2P_{1/2}$ rather than the lower-energy component $^2P_{1\frac{1}{2}}$. To the present writer it has always seemed strange that so relatively minor a constitutional difference as that between the two sublevels of a ^2P state should have any fundamental connection with a constitutional difference presumably so pronounced, and so different in character, as that between an ion-molecule and an atom-molecule.

In previous papers by the writer,[4] special reasons why molecules of the special types X_2 and XY give predominantly one excited ($^2P_{1/2}$) atom on photodissociation have been analyzed, thus showing why Franck's criterion can hold in those cases; but as was noted above, it is now improbable that the criterion actually *does* hold in all such cases. In the present paper a further systematic and comparative study and theoretical interpretation of absorption spectra is made, extending to the types HX, AgX and MX.

From the present work and that already done on X_2 and XY, it is concluded that the usual validity of Franck's criterion in molecules AX is due rather to a combination of special and distinctly fortuitous circumstances than to a general theoretical cause. It is found that in all molecules AX, both atom-molecules and ion-molecules, absorption processes giving photodissociation into unexcited A plus X($^2P_{1\frac{1}{2}}$) must occur; but that in the case of many but not all atom-molecules, the absorption coefficient for such processes happens to be unusually low (cf. the postulates in Section 4); while in the case of ion-molecules (of which the only known representatives are of the type MX) the absorption coefficient for such processes is always fairly large, in consequence partly or perhaps mainly of the characteristic case *c* nature of the excited states of these ion-molecules. Further reference to Franck's criterion will not be made in later sections of this paper, but the nature of its explanation can be seen by a study of these sections of the paper and of similar work on X_2 and XY.

On the basis of their spectroscopic criterion, Franck and Kuhn[5, 6] class HI and AgX (other than perhaps AgF) as atom-molecules, MX as ion-molecules. Data on AgF are not available, but it seems possible that it may be an ion-molecule like MX. From quantum-mechanical considerations, Pauling[7] and others conclude that all HX are atom-molecules. Even though AgX are atom-molecules, it would probably be generally agreed that they have more ionicness than HX, and so are intermediate in character between HX and MX (cf. Table II of I, also Figs. 1–3). The present study of the several spectra supports this idea.

3. Coupling Cases and Correlation Rules for AX Molecules

In molecules AX, namely HX, AgX and MX, we expect to find energy levels *N*, *T* and *V* just analogous to those which are found in H_2, M_2 and MH (cf. I and II), and in addition we expect the *Q* group of levels (cf. Table I of I). This group consists of states $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_{0^-}$ and $^3\Pi_{0^+}$, and $^1\Pi$, with energy expected usually to increase in the order named. These designations, however, are really appropriate only if the spin-orbit coupling is of the ordinary case *a* or case *b* type (Λ-Σ coupling). We shall, nevertheless, for the sake of convenience and simplicity, use these same designations, so far as possible, even when the coupling is of another type.

Before considering the individual spectra of HX, AgX and MX, it is advisable to make a survey of the energy relations and other properties to be expected for the *Q* group of levels (cf. Tables I–IV in I and II for a partial summary). In doing this, one soon finds that it is necessary to consider several different types of spin-orbit coupling. This is partly because the predominant type of coupling varies from one molecule to another, and partly because for any given molecule the coupling varies with the internuclear distance *r*. A thorough knowledge of the

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[5] J. Franck and H. Kuhn, Zeits. f. Physik **43**, 164 (1927): AgI, HI.

[6] J. Franck and H. Kuhn, Zeits. f. Physik **44**, 607 (1927): AgCl, AgBr; B. A. Brice, Phys. Rev. **33**, 1090 (1929); **35**, 960 (1930); **38**, 658 (1931); A. Terenin, Physica **10**, 209 (1930): AgI; H. Kuhn, Zeits. f. Physik **63**, 458 (1930); M. Ashley and F. A. Jenkins, Phys. Rev. **37**, 1712*A* (1931); **42**, 438 (1932).

[7] L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932); F. Hund, Zeits. f. Physik **40**, 762 (1927).

electronic states of a molecule requires understanding them over a range of r values. For dissociation correlations one must cover the range of r from r_e to ∞.

Because of the need of considering several coupling cases, and the rules of correlation between them, the explanations of the observed spectra become of necessity somewhat complex. Although this is regrettable, it appears to be an unavoidable consequence of the actual complexity of the underlying molecular situation.

The main types of coupling which we need to consider are three: (1) Λ, Σ coupling; (2) Ω, s coupling;[4] (3) the writer's case c coupling,[8] i.e., the "far-nuclei" variety of case c coupling. Types (1) and (2) are possible for moderate r values, while type (3) occurs for large or in some cases also for moderate r values. For stable molecular states, and for some unstable ones, the choice is between (1) and (2). Then if spin-orbit coupling is relatively weak, we have Λ, Σ coupling, if strong, we have Ω, s or some similar coupling. For molecules which are essentially just pairs of atoms interacting weakly (this includes *all* molecules for sufficiently large r values), we have type (3). There is a fourth type of coupling (Hund's case c coupling, or "close-nuclei" variety of case c) which will be discussed in Section 5 in connection with the behavior of the HX energy levels as $r\rightarrow 0$, but this is not important for AgX or MX, and will not be considered in this section.

In coupling types (1) and (2), the Q group of levels can be considered by itself. In type (3), however, we shall find it necessary to consider N, T, V, and Q (or at least T, V and Q) together, since in this case they become, so to speak, mutually entangled.

For ordinary Λ-Σ coupling, the levels ${}^3\Pi_2$, ${}^3\Pi_1$, ${}^3\Pi_0$ of the Q group should be equally spaced with intervals ${}^3\Pi_0-{}^3\Pi_1$ and ${}^3\Pi_1-{}^3\Pi_2$ each equal to about $(1/2)a$, where a is the spin-orbit coupling coefficient of the X atom, in its normal electron configuration; a should be about 2/3 of the ${}^2P_{1/2}-{}^2P_{3/2}$ separation of the latter.[4] The ${}^1\Pi$ level should be considerably higher in energy.

If, however, as in the levels of X_2 and XY which are analogous to the present Q group, there should be a strong tendency toward Ω-s coupling,[4] then the levels ${}^3\Pi_2$, ${}^3\Pi_1$ should form a doublet of width much less than $a/2$, separated by an interval of about a or a^+ from the levels ${}^3\Pi_0$, ${}^1\Pi$, which should also form a doublet ($a=a^+$ of X^+ ion[4]). The two doublets should then, respectively, be thought of in AX as

$$[(\sigma^2\pi^3,\ {}^2\Pi_{3/2})\sigma^*]_{2,\ 1} \quad \text{and} \quad [(\sigma^2\pi^3,\ {}^2\Pi_{1/2})\sigma^*]_{0,\ 1},$$

the final subscripts giving resultant Ω values. In ideal Ω-s coupling, each doublet width would shrink to zero. As we shall see below, the actual coupling in the HX molecules, for r near r_e of state N, probably approximates the Ω-s type.

The third possible kind of coupling, which apparently is closely approximated in the excited states of the MX molecules, is the writer's "case c" or "far-nuclei" type.[8] In this the combination between the atoms is loose, and each atom A preserves its own internal coupling and its resultant J_A. The interatomic forces, however, cause a space quantization of each J_A relative to the internuclear axis, giving a quantum number Ω_A for each atom.

In the MX excited states in which we shall be interested, the M atom is in its normal state $\ldots ms$, ${}^2S$, while the X atom is in one of the two states ${}^2P_{3/2}$ and ${}^2P_{1/2}$ of the atom's normal electron configuration $\ldots np^5$. Thus $J_M=1/2$ and $J_X=3/2$ or $1/2$. When $J_M=1/2$ and $J_X=3/2$, we have $\Omega_M=1/2$, with Ω_X either 3/2 or 1/2; when $J_M=1/2$ and $J_X=1/2$, we have $\Omega_M=1/2$, $\Omega_X=1/2$. There is now in each case a small interaction between Ω_M and Ω_X to give a resultant Ω of the molecule as a whole. The possible Ω resultants are as follows:[8] from M plus ${}^2P_{3/2}$ of X, $\Omega=2$, 1, 1, 0^+, 0^-; from M plus ${}^2P_{1/2}$ of X, $\Omega=1$, 0^+, 0^-.

Of these several case c electronic states, only $\Omega=2$ can be correlated uniquely with a single definite state, namely ${}^3\Pi_2$, of the other coupling cases. The three states $\Omega=1$, *taken collectively*, do, however, correspond to the Q states ${}^3\Pi_1$, ${}^1\Pi$ and the $\Omega=1$ component[8] of the $T\,{}^3\Sigma^+$ state. The correspondence consists essentially in the fact that the wave functions of the three $\Omega=1$ states of pure case c can be expressed as linear combinations of the wave functions of the three Λ-Σ coupling states just mentioned, and *vice versa*.

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[8] R. S. Mulliken, Rev. Mod. Phys. **3**, 113–119 (1931); **4**, 20, 26–29 (1932). For some case c energy formulas, cf. J. H. Van Vleck, Phys. Rev. **40**, 568 (1932).

In a similar manner the two pure case c states $\Omega=0^+$ together correspond to the Λ-Σ coupling states $Q\,{}^3\Pi_{0^+}$ and $V\,{}^1\Sigma^+$. Similarly, the two 0^- states together correspond to the $Q\,{}^3\Pi_{0^-}$ and the 0^- component[8] of $T\,{}^3\Sigma^+$.

For each of the above three coupling schemes, there is a one to one correspondence between, on the one hand, the set of states $\mathrm{A}({}^2S)+\mathrm{X}(p^5, {}^2P_{3/2})$, $\mathrm{A}(s, {}^2S)+\mathrm{X}(p^5, {}^2P_{1/2})$, and $\mathrm{A}^++\mathrm{X}^-(p^6, {}^1S)$, existing at $r=\infty$, and, on the other hand, the set of molecular states $N\,{}^1\Sigma^+$, $T\,{}^3\Sigma^+$, $Q\,{}^{1,3}\Pi$, and $V\,{}^1\Sigma^+$ or their case c equivalents. In all the coupling cases, the sets T and Q are correlated with $\mathrm{A}(s, {}^2S)+\mathrm{X}(p^5, {}^2P_{3/2,\,1/2})$. The allegiances of N and V on dissociation, however, are found to be less definite. In MX, N goes to $\mathrm{M}^++\mathrm{X}^-$, and V (mixed with $Q\,{}^3\Pi_{0^+}$) goes with T and Q to $\mathrm{M}+\mathrm{X}$. In HX and AgX, N goes with T and Q to $\mathrm{A}+\mathrm{X}$, while V goes to A^++X^-. These results concerning the correlations of N and V on dissociation are based (see below) on theoretical considerations and on band spectra.

4. Special Postulates for AX Molecules

In interpreting and drawing conclusions from the observed spectra of HX, AgX and MX, it will be helpful to refer to some conclusions reached previously in studying the X_2 and XY spectra.[4] The lowest observed excited levels of these molecules belong to a group analogous to the present Q group. Taking ICl as an example, and calling the lowest states N and Q in analogy to the present case, we had:

$$\begin{aligned} &N\colon\ (\sigma_{\mathrm{ClI}})^2(\pi_{\mathrm{Cl}})^4(\pi_{\mathrm{I}})^4,\ {}^1\Sigma^+;\\ &Q\colon\ (\sigma_{\mathrm{ClI}})^2(\pi_{\mathrm{Cl}})^4(\pi_{\mathrm{I}})^3\sigma^*_{\mathrm{ICl}},\ {}^{1,3}\Pi. \end{aligned} \tag{1}$$

States N and Q of ICl are very much like those of HX (cf. Table I of Paper I), except for the presence of an extra group of nonbonding π electrons (π_{Cl}),[4] which need not concern us here.

In ICl, and in XY and X_2 generally, it was found that the strongest transitions between N and group Q are often or usually those to the ${}^3\Pi_{0^+}$ component of this group, *which for brevity we shall hereafter refer to* as Q_0. It was concluded that transitions to the ${}^1\Pi$ (and ${}^3\Pi_1$) must often or usually be inherently weak. The coupling in the Q states of X_2 and XY is mostly intermediate in type between Ω-s and case c. In either of these cases, the spectroscopic properties of ${}^1\Pi$ should be shared more or less completely by ${}^3\Pi_1$, since the wave functions of pure singlet and triplet type which would exist for Λ-Σ coupling become mixed together in either Ω-s or case c coupling. [In case c, $\Omega=1$ of ${}^3\Sigma^+$ is also mixed in, as described above.]

The rather high intensity of the spectroscopic transition from N to Q_0 in I_2 was attributed by Van Vleck to the existence of a strong perturbation of Q_0 by a higher lying ${}^1\Sigma^+$ state of such a nature as to have the ability to receive strong spectroscopic transitions from N. Such a perturbation is especially likely in case c, and this admixture of ${}^1\Sigma^+$ wave function would impart to Q_0 the power to combine strongly with N. The higher ${}^1\Sigma^+$ in question was tentatively identified by Van Vleck as the D state of I_2. The writer then pointed out that this "D" state is very probably the expected largely ionic state analogous to the V state of H_2. Strong perturbation of Q_0 by V may then be tentatively considered, for X_2 and XY, as the, or at least a, cause of the strong combination of N with Q_0.

Another possible cause was suggested and favored by the writer,[4] on the ground that a perturbation of Q_0 by V so strong as to give rise to the very high observed intensity of $Q_0\leftarrow N$ in I_2 (cf. reference 4, Table IIB) should cause a depression of the energy of Q_0 relative to ${}^3\Pi_1$ larger than would be compatible with the observed relative energies of ${}^3\Pi_1$ and Q_0 (cf. reference 4, Table IIA). The writer's suggested cause would not depress Q_0 at all. Reconsideration of the matter indicates, however, that the argument is not conclusive. If it be assumed, for instance, that the electric moment of $V\leftarrow N$ has a value corresponding to a displacement of a charge e by 10^{-8} cm, then a 25 percent admixture of V wave function in Q_0 will account for the observed intensity of $Q_0\leftarrow N$; and estimating the energy interval from Q_0 to V as 4 ev, one finds by perturbation theory that Q_0 should be pushed down by about 0.25 ev. This is indeed rather large, but it may be that there is enough uncertainty in respect to the observed ${}^3\Pi_1-Q_0$ separation, the exact nature of the coupling, and the size of the $V\leftarrow N$ electric moment, to make such a result admissible. A further possibility might be that Van Vleck's cause and the writer's cause for the strength of $Q_0\leftarrow N$ operate simultaneously in the case of I_2, in which case both effects could be fairly strong without much depression of Q_0. In any case, it is to be noted that the writer's suggested cause is dependent on the presence of *two* groups of π electrons, and so would be inapplicable to explain high intensity of $Q_0\leftarrow N$, if this occurs, in HX, AgX or MX. Van Vleck's cause would, however, still be operative.

The foregoing discussion suggests that the following trial postulates form a reasonable tentative basis for interpreting the spectra of HX, AgX and MX. (1) Transitions between the atomic and ionic $^1\Sigma^+$ state, i.e., $V \leftarrow N$, are always intrinsically very intense. (2) Transitions from N to the $^1\Pi$ and $^3\Pi_1$ components of Q may often be intrinsically weak in these molecules, as is often or usually the case in X_2 or XY. (3) Transitions $Q_0 \leftarrow N$ can be strong because Q_0 may be strongly perturbed by V if strong case c tendencies are present.

Justification for these postulates is as follows. Postulate (1) is theoretically very reasonable, and is supported, experimentally, by the existence of strong transitions $V \leftarrow N$ in H_2, MH and I_2. Postulate (2) is theoretically possible, although not obviously necessary. Its chief basis is its experimental validity for X_2 and XY. This makes it tenable, although not definitely predictable, for any or all of the types HX, AgX and MX. The justification of (3) is similar to that of (2), namely theoretical admissibility and experimental validity in the cases of X_2 and XY.

Anticipating our application of the foregoing postulates in Sections 5–7, it may be well to report here the not very surprising and indeed rather gratifying fact that, in practice, we are forced to conclude that the somewhat arbitrary and special postulates (2) and (3), which are based on experience with halogen molecules, probably are honored as much in the breach as in the observance.

5. The Molecules HX

No discrete electronic band spectra of neutral HX have been found at wave-lengths above λ2000. Continuous absorption and emission bands are, however, found in the ultraviolet. Whether or not the recorded continuous emission bands[10] correspond in part to the same electronic transitions as are involved in the absorption bands appears uncertain. In the following, we shall consider only the absorption bands, since they surely arise from the normal electronic state.

The absorption spectra of HI, HBr and HCl all show absorption beginning in the ultraviolet and reaching a maximum near λ2000. In HF, there is no appreciable absorption at wave-lengths greater than λ1900 or less.[11] In HCl, Leifson[12] reports a broad maximum of absorption at about λ2000, followed by others at about λ1700 and below. More attention has been devoted to HBr and HI; the best results appear to be those published recently by Goodeve and Taylor,[13] who have made quantitative measurements of the absorption coefficient of HBr down to about λ1850 and of HI apparently to about λ2300; quantitative data of others on HI go to about λ2200.[13a] The measurements in each case unfortunately stop just short of the maximum of the absorption curve. The maximum is estimated to come at about λ1790 for HBr ($\nu = 56{,}000$) and at about λ2200 for HI ($\nu = 45{,}000$). The maximum in each case is broad and flat.[13a]

Defining the absorption coefficient k by $I = I_0 e^{-kl}$ (l = path in cm; gas density corrected to 0°C, 760 mm), one finds by calculation from the results of Goodeve and Taylor on HBr, $k_{\max} = 56$. [The absorption coefficients given by Goodeve and Taylor, according to a private communication from Dr. Goodeve, refer to gas at 17°C.] On the long wave-length side of the HBr curve, k has fallen to about half its maximum value at about $\nu = \nu_{1/2\ \max} = 49{,}450$. Assuming that the absorption curve is somewhat less steep on the high frequency than on the low frequency side, as would be expected, and then proceeding in the manner outlined in Table IIB of a previous paper[4] on the halogens X_2 and XY, one finds approximately for the effective electric moment amplitude P associated with the transition, the value $P/e = 0.24 \times 10^{-8}$ cm. This is approximately the same as for the strong visible I_2 absorption system ($P/e = 0.26 \times 10^{-8}$ cm) and stronger than for the corresponding Br_2 transition ($P/e = 0.13 \times 10^{-8}$ cm).

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[10] M. Kulp, Zeits. f. Physik **67**, 7 (1931): HCl; A. K. Dutta and S. C. Deb, Zeits. f. Physik **93**, 127 (1934). Cf. also H. C. Urey and J. C. Bates, Phys. Rev. **34**, 1541 (1929): but probably X_2 not HX; and W. Weizel, H. W. Wolff, and H. E. Binkele, Zeits. f. physik. Chemie **B10**, 459 (1930): HBr, but probably not involving the normal state.

[11] Cf. H. J. Plumley, Phys. Rev. **49**, 405L (1936); K. Siga and H. J. Plumley, Phys. Rev. **48**, 105L (1935).

[12] S. W. Leifson, Astrophys. J. **63**, 73 (1926).

[13] C. F. Goodeve and A. W. C. Taylor, Proc. Roy. Soc. **A152**, 221 (1935); **A154**, 181 (1936); and references given there.

[13a] Recently H. J. Plumley in this laboratory has photographed the HI absorption down to about λ1950. The maximum of the absorption appears to be (very roughly) near λ2300, and there appears to be no evidence of more than one maximum. Quantitative measurements from λ2300 down would, however, be desirable.

In the case of HI, $k_{\max}$ is 16 according to the data of Goodeve and Taylor, *less* than for HBr. Proceeding in the same manner as above, one finds $P/e=0.14\times10^{-8}$ cm for HI, about the same as for the Br_2 transition. The fact that the transition probabilities increase from Br_2 to I_2, but decrease from HBr to HI, indicates that the nature of the transition or transitions in HX may be considerably different than in X_2.

It has been shown, especially by Goodeve and Taylor, that the long wave-length tails of the HBr and HI continua cannot be ascribed primarily to initially vibrating molecules. This is important in relation to the dissociation process to which these continua must correspond. The dissociation energy of HI into $H+I(p^5, {}^2P_{3/2})$ is 3.02 ev, corresponding to λ4080; for $H+I(p^5, {}^2P_{1/2})$ it is 3.96 ev, or λ3120. Absorption is found to be very appreciable to well beyond λ3120 and has been followed to beyond λ3600 with long gas columns. Hence, noting also that no discrete bands are observed,[13] so that it cannot be a question of a curve going down to a minimum and then rising to $H+I({}^2P_{1/2})$, it is clear[13] that at least a considerable part of the continuous absorption in HI gives rise to $H+I({}^2P_{3/2})$, i.e., to unexcited atoms. But further, the absorption intensity in the tail shows no noticeable acceleration in its rate of following off beyond λ3120; this tends to indicate that *most* or perhaps even nearly all of the absorption at all wave-lengths is associated with a potential energy curve or curves dissociating into $H+I({}^2P_{3/2})$. The data on HBr, although less adequate, point to similar conclusions.

We shall now consider how the foregoing and other experimental evidence may be interpreted in the light of the tentative postulates stated at the end of Section 4. First of all, it is clear that the observed continuum cannot represent transitions $V\leftarrow N$. One can estimate the position of the V level (cf. Pauling's curves[7] for HX) and it is too high. Besides, V should be a stable level and so $V\leftarrow N$ should give discrete bands. Further, the levels Q should certainly lie well below T and V according to band spectrum data on HX^+ (cf. discussion in a later paragraph in connection with Fig. 1), so that $Q\leftarrow N$ absorption might be expected at longer wave-lengths than either $T\leftarrow N$ or $V\leftarrow N$. $T\leftarrow N$ should give continuous absorption, but faint unless case *c* tendencies are strong, which is not likely here (see below). The observed continuum may then safely be attributed to $Q\leftarrow N$; more specifically, to transitions from N to ${}^3\Pi_1$, ${}^3\Pi_{0^+}$, and ${}^1\Pi$ of Q, transitions ${}^3\Pi_2\leftarrow N$ and ${}^3\Pi_{0^-}\leftarrow N$ being rigorously forbidden.

It appears possible that in HX all the transitions ${}^3\Pi_1\leftarrow N$, Q_0 (i.e., ${}^3\Pi_{0^+}$)$\leftarrow N$, and ${}^1\Pi\leftarrow N$ may contribute appreciably to the observed continuum under discussion. The extreme long wave-length part, or tail, of the HI absorption, however, cannot belong to $Q_0\leftarrow N$, since Q_0 necessarily gives $H+I({}^2P_{1/2})$ on dissociation; hence the tail must belong to ${}^3\Pi_1\leftarrow N$ or ${}^1\Pi\leftarrow N$ or both. Either of the two following possibilities then appears compatible with the existing data:

(a) ${}^3\Pi_1\leftarrow N$ and ${}^1\Pi\leftarrow N$ much exceed $Q_0\leftarrow N$ in total intensity;

(b) ${}^3\Pi_1\leftarrow N$ plus ${}^1\Pi\leftarrow N$ about equal $Q_0\leftarrow N$ in total intensity. A third possibility (c) that $Q_0\leftarrow N$ much exceeds the other two in total intensity, is probably incompatible with the evidence (see below).

In order to discuss these possibilities intelligently, it is necessary to consider what kind of coupling (cf. Section 3, above) is to be expected in the states ${}^3\Pi_1$, ${}^1\Pi$, and Q_0, for r values near r_e of state N, from which the absorption processes start. From the character of the HI and HBr continua (great breadth, indicating steeply rising $U(r)$ curves[13] at r equal to r_e of N; and intensity maximum at a frequency corresponding to 2 or 3 ev above the possible asymptotes of the $U(r)$ curves) it is clear that at $r=r_e$ of N there is strong interaction between the two atoms H and X. This and other considerations remove the possibility that the coupling is predominantly of the case *c* separated-atom type, except for large r values. In view of the large multiplet intervals in the Br and I atoms, we may conclude that the coupling in HBr and HI is predominantly of the Ω-*s* (*Jj*-like) type, possibly modified by some tendency toward case *c*. Predominant Ω-*s* coupling probably exists also in HCl and perhaps even in HF, since the relatively high excitation energy of the excited electron makes the electronic states of these molecules comparable with those of the atoms argon and neon.

With Ω-*s* coupling,[4] the levels ${}^3\Pi_1$ and ${}^1\Pi$ in HI should be separated by about 0.6 ev, and the Q_0

level should be close to the $^1\Pi$. As $r \rightarrow \infty$, however, we go over to case c coupling, and the $^3\Pi_1$ and $^1\Pi$ should draw together and both dissociate into $H+I(^2P_{3/2})$, while the Q_0 must go to $H+I(^2P_{1/2})$. With Ω-s coupling, transitions to the $^3\Pi_1$ and $^1\Pi$ should be about equally strong, since really the singlet-triplet distinction is completely broken down.

Returning to the possibilities (a), (b), (c) mentioned above, we now see that if (a) is correct, the observed absorption curve in HI must represent mainly the superposition of two similar absorption curves with maxima about 0.6 ev apart. If possibility (b) is correct, there must be three superposed curves, of which $Q_0 \leftarrow N$ and $^1\Pi \leftarrow N$ should have their maxima close together, with $^3\Pi_1 \leftarrow N$ at about 0.6 ev longer wave-length. If (c) should be correct, the absorption curve would be essentially a curve $Q_0 \leftarrow N$ with a single maximum, but with two curves $^3\Pi_1 \leftarrow N$ and $^1\Pi \leftarrow N$ superposed on it, both much weaker than $Q_0 \leftarrow N$ but still strong enough to account for the observed long wave-length tail of the absorption. This, however, is hardly possible, since the intensity of the tail fits on too smoothly to that of the main part of the absorption (see above). Hence possibility (c) is probably excluded on this ground.

Possibilities (a) and (b) require the presence of two strong maxima 0.6 ev apart, while what has been observed experimentally is a single very broad maximum.[13a] However, examination of the observed curve indicates that it could easily be the resultant of two broad-topped curves with their maxima as much as 0.6 ev apart. All things considered, the existing data on HI appear to be compatible with either of the two possibilities. The same is true of HBr and HCl, where, moreover, the maxima of various absorption processes, if more than one should be intensely present, would be closer together than in HI.

Besides the reason already given against possibility (c), it should be noted that this possibility would be expected only if the coupling tended strongly toward case c; but this, as we have already seen, is improbable. Moreover, the fact that the absorption is stronger in HBr than in HI disfavors possibility (c), since any case c tendencies should be stronger in HI than in HBr. In this connection, a comparison with the cases of Br_2 and I_2 is instructive: the absorption is much weaker in Br_2 than in I_2; the high intensity in I_2 is attributed to strong case c influence which, together with weakness of $^3\Pi_1 \leftarrow {}^1\Sigma^+$ and $^1\Pi \leftarrow {}^1\Sigma^+$, is expressed in the realization of possibility (c); in Br_2, on the other hand, we have probably more nearly possibility (b).[4] Thus in the molecules HX, possibilities (a) and (b), or something between, appear by far the most probable, with the chances for (b) greatest for HI.

Goodeve and Taylor, assuming that essentially a single upper electronic state is involved in the continuous absorption of HX above λ2000, have constructed a $U(r)$ curve for this state in the same manner as was done by Gibson, Rice, and Bayliss for Cl_2, by a quantum-mechanical treatment of the curve of absorption coefficient against frequency. From the discussion in the preceding paragraphs, however, it will be seen to be very probable that more than one upper $U(r)$ curve is importantly involved in the absorption. If so, the $U(r)$ curve given by Goodeve and Taylor represents some sort of average over the actual curves. Here it may also be noted that the smoothness of the effective curve obtained by Goodeve and Taylor strongly disfavors possibility (c).

Fig. 1 illustrates the nature of the $U(r)$ curves for states N, Q, T and V of HI, the Q curves $^3\Pi_1$ and $^1\Pi$ being drawn so that their average agrees approximately with Goodeve and Taylor's curve. The positions of the states $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$, and $^1\Pi$ are estimated assuming Ω-s coupling.[4] The heights of the T and V states above the Q states have been estimated as follows. In the cases of HCl^+ and HBr^+, the energy interval from the normal state $\sigma^2\pi^3$, $^2\Pi$ to the excited state $\sigma\pi^4$, $^2\Sigma^+$ is known experimentally from band spectra. From these values for HCl^+ and HBr^+ (about 3.5 ev in both cases), we can estimate the corresponding interval for HI^+, which is not known experimentally, as 3.6 ev. Now the electron configuration $\sigma\pi^4\sigma^*$ of the states T, V of neutral HI differs from the configuration $\sigma^2\pi^3\sigma^*$ of states Q in exactly the same way that the configuration $\sigma\pi^4$ of the excited $^2\Sigma^+$ of HI^+ differs from the configuration $\sigma^2\pi^3$ of the $^2\Pi$ normal state of HI^+. Hence, for comparable r values (say r_e of $^2\Pi$ of HI^+, which is nearly the same as r_e of state N of HI), the energy difference should be nearly the

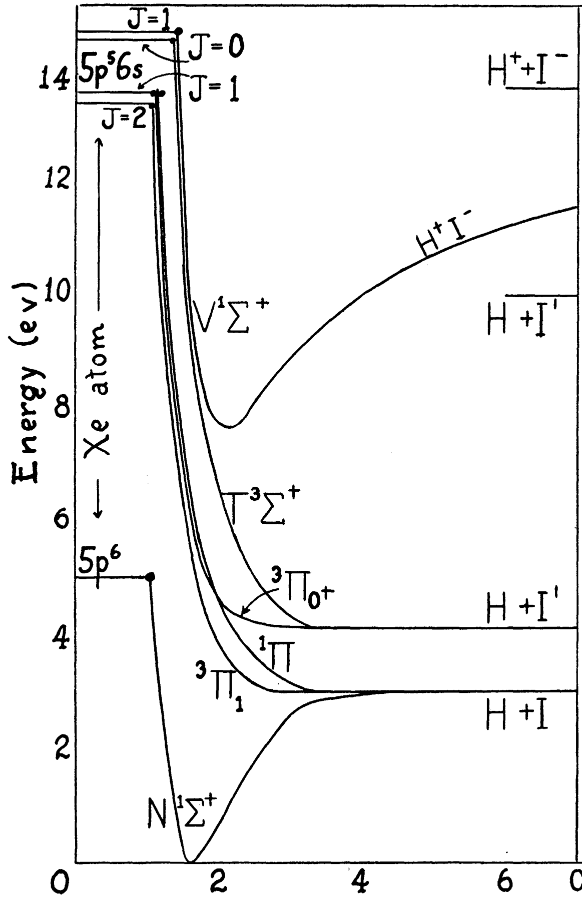

Fig. 1.

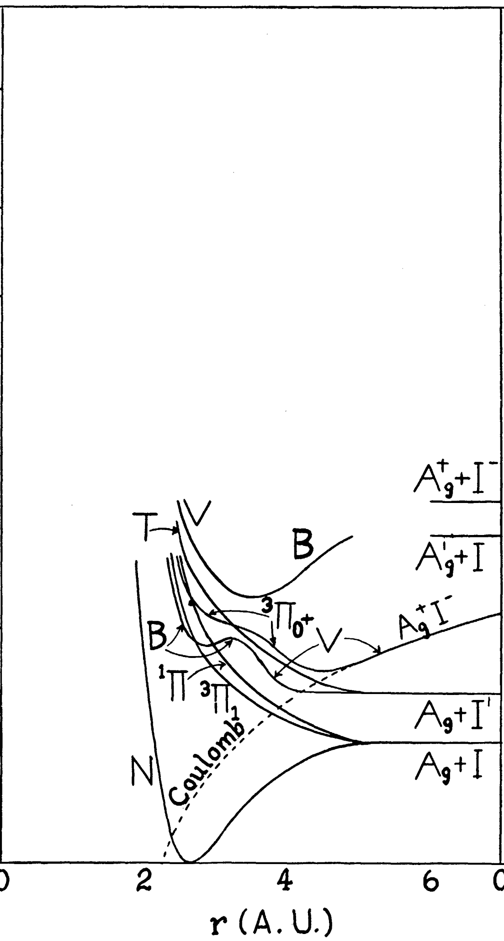

Fig. 2.

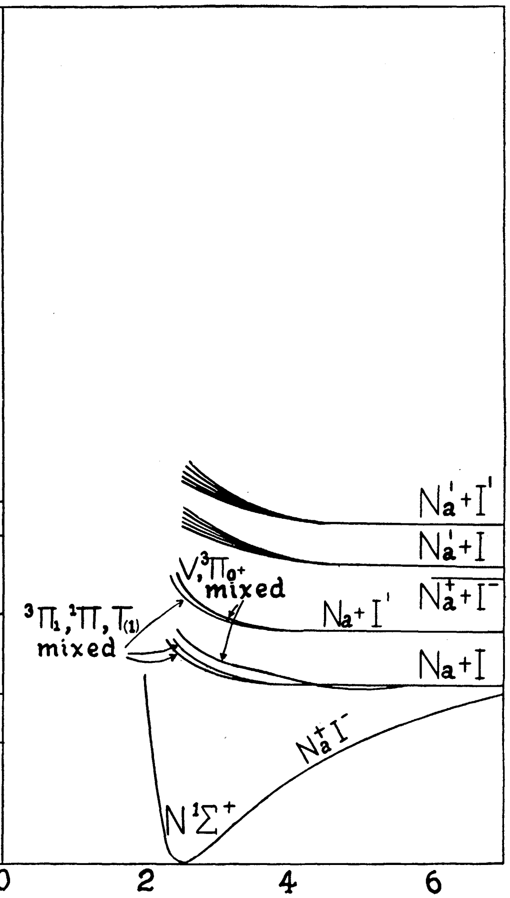

Fig. 3.

same between the center of gravity of the group Q and that of T, V in HI as between the two states of HI$^+$. The value 3.5 ev has been assumed in Fig. 1. The mode of dissociation of each of the various individual Q, T sublevels is determined in accordance with the usual case c rules[8] (cf. summary in Section 4). The V level in Fig. 1 is drawn somewhat above the T level at small r, and with the usual ionic type of $U(r)$ curve for larger r; as in the case of other V states, however (cf. I, II), dissociation actually takes place probably into a normal H plus an excited I$(5p^46s)$ atom rather than into two ions. In the neighborhood of the V state, and higher, other levels not shown in Fig. 1 are to be expected. These would be in part analogous to the levels $\sigma^2\pi^4\pi^3\sigma^x$ and others of e.g., ICl (cf. reference 4, Table IV).

In seeking a thorough understanding of the electronic structures and potential energy curves of states N, Q, T, and V of HX, it is valuable to follow them all the way from $r=0$ to $r=\infty$. Consideration of the united-atom ($r=0$), while not in general very important, is of real value for hydride molecules.

A clearer picture can be obtained if at first we neglect, for all values of r, the complicated patterns of energy sublevels corresponding to the various orientations of spin and orbital angular momentum vectors. Starting from $r=0$, we then find (cf. I, Table 1) that . . . $5p^6$, ^1S of Xe ($r=0$) goes over into . . . $\sigma^2\pi^4$, $^1\Sigma^+$ of HI ($r=r_e$) and this into $5p^5$, ^2P of I plus $1s$, ^2S of H ($r=\infty$). Further, . . . $5p^56s$, $^{3,1}P$ of Xe splits into $\sigma^2\pi^3\sigma^*$, Q $^{1,3}\Pi$ and $\sigma\pi^4\sigma^*$, $^{1,3}\Sigma^+$ (T and V) of HI; for large r values Q and T, like N, go over into $5p^5$ of I plus $1s$ of H, while V goes (or tends to go) into H$^+$ plus $5p^6$ of I$^-$.

At $r=0$, levels Q, T and V are about 9 ev above N; at r near r_e of state N, Q is about 5.6 ev above N, while T and V are about 9 ev above N according to Fig. 1; at $r=\infty$, N, Q and T coincide, while V is 10.3 ev higher. Attention should be called to the energy intervals from N to Q, T and V, which are already two-thirds as large as at $r=0$ for $Q-N$, and probably fully as large as at $r=0$ for $T-N$ or $V-N$. From these one may reasonably conclude that the actual structure of the molecule for r values near r_e of N can be better approximated in terms of united-

FIG. 1. Potential energy curves for lowest electronic states of HI. The curve for state N is based on spectroscopic and chemical data. The approximate locations of the Q curves (marked $^3\Pi$ and $^1\Pi$ in the figure) are based on spectroscopic data. Further details of the Q curves, and the forms of the T and V curves, are uncertain, but have been estimated (cf. text) in accordance with theoretical considerations and with band spectrum data on HCl$^+$ and HBr$^+$. At the left an extra scale, referring to the Xe atom, is added, and the state of the Xe atom into which each of the HI curves would go as $r\rightarrow 0$ is indicated. The Q curves $^3\Pi_2$ and $^3\Pi_0{}^-$ have been *omitted;* the former should be slightly below $^3\Pi_1$, the latter slightly below $^1\Pi$; both should go into the lowest excited level of the Xe atom as $r\rightarrow 0$. For $r=\infty$, I refers to I$(p^5, {}^2P_{\frac{1}{2}})$, I′ to I$(p^5, {}^2P_{1\frac{1}{2}})$ or (upper level H+I′) to I$(p^4s, {}^4P_{2\frac{1}{2}})$.

FIG. 2. Potential energy curves for lowest electronic states of AgI. The curves for states N and B are based on spectroscopic data and on the chemical dissociation energy (2.04 ev) for state N; the value of r_e for state N was estimated by the use of Badger's rules, and that of state B from that of state N by interpreting the intensity distribution in the $B\leftarrow N$ bands and continuum in terms of the Franck-Condon principle. The $^3\Pi_2$ and $^3\Pi_0{}^-Q$ curves (*not shown*) should be slightly below the $^3\Pi_1$ and $^1\Pi$, respectively. The curves for states B, $^3\Pi_0{}^+$, and V are drawn in a plausible way, corresponding to an interpretation suggested in the text. All the curves are strongly uncertain, except in part those of N and B near their r_e's. The labels B, $^3\Pi_0{}^+$, and V are shifted about from one curve to another with changing r in such a way that a given label always corresponds to a wave function approximately of a given character (see text). In regard to certain difficulties about the $^3\Pi_1$ and $^1\Pi$ curves, see the third from last paragraph of Section 6. The dashed curve marked "Coulomb" shows how the energy of Ag$^+$I$^-$ would run if there were a pure Coulomb attraction. At $r=\infty$, Ag′ refers to Ag(^2P), I′ to I$(^2P_{\frac{1}{2}})$.

FIG. 3. Potential energy curves for lowest electronic states of NaI. The approximate curve shown for state N follows the law $U(r)=(-e/r)+(\beta/r^n)$, with $\beta=3940$ and $n=9.5$ (energy in ev and r in A), β and n being approximately the same as in the Born formula for the lattice energy of NaI crystals; the constant β has, however, been adjusted to correspond to a dissociation energy (into ions) of 5.00 ev, based on chemical and spectroscopic data.[19] The other curves have been estimated in accordance with considerations described in the text. Because of the dominance of case c coupling here (unlike Figs. 1, 2), the states $Q(^3\Pi$ and $^1\Pi)$, $T(^3\Sigma^+)$, and $V(^1\Sigma^+)$ no longer exist as such. Instead we have two 0^+ states (i.e. case c states with $\Omega=0$, and plus character), whose wave functions can be expressed as mixtures of Q $^3\Pi_0{}^+$ and V $^1\Sigma^+$; further, three 1 states (i.e., $\Omega=1$) representing mixtures of Q $^3\Pi_1$, Q $^1\Pi$, and an $\Omega=1$ component of T $^3\Sigma^+$; and so on. The approximate heights of the curves for r equal to r_e of N are based on spectroscopic information. The relative spacings and positions of the 0^+ and 1 state curves forming each bundle are uncertain, but are shown in a plausible way. The bundle from Na(^2S)+I$(^2P_{1\frac{1}{2}})$ should contain two additional curves (a 2 and a 0^-) which are not shown; that from Na(^2S)+I$(^2P_{\frac{1}{2}})$ should contain one 0^- which is not shown. The bundles from Na(^2P)+I are indicated only roughly; each should contain a number of curves. For $r=\infty$, Na′ means Na(^2P), I′ means I$(^2P_{\frac{1}{2}})$.

atom orbitals than of separate-atom orbitals. This strong tendency toward united-atom conditions, together with the rather large interval between $5p^6$ and $5p^56s$ of Xe, may be said to account for the pronounced repulsive character of the $U(r)$ curves of the Q (and T) states of HI (cf. also Dutta and Deb[10]).

Starting from the united-atom, where T, V, Q all belong to $5p^56s$ and coincide, a separation of about 3.5 ev between Q and T, V is attained for r near r_e of N. This separation may be said to be due to the *molecularization* of the Xe orbitals, whereby $5p^56s$ gives rise to $\sigma^2\pi^3\sigma^*$ (Q) or to $\sigma\pi^4\sigma^*$ (T, V). The molecular orbitals σ, π, which for $r=0$ are $5p\sigma_{\text{Xe}}$, $5p\pi_{\text{Xe}}$ and are equal in energy, now come to differ in energy by about 3.5 ev.

For r near r_e of N, the use of true molecular orbitals here obviously corresponds to a better approximation than the use of united-atom orbitals. It appears reasonable also, in view of the energy relations for the Q, T and V states, to believe that molecular orbitals give a better approximation here than separate-atom atomic orbitals. At larger r values, however, the value of molecular orbital approximations gradually, so to speak, dissolves, and atomic orbital configurations $5p_{\text{I}}{}^5\cdot 1s_{\text{H}}$ and $5p_{\text{I}}{}^6$ become appropriate. For moderately large r values short of $r=\infty$, the $5p_{\text{I}}$ orbital type is subdivided into $5p\sigma_{\text{I}}$ and $5p\pi_{\text{I}}$. It is interesting to note how the states Q and T, which both belong to $5p^56s$ of Xe at $r=0$ but spread apart in energy at moderate r values, come together again at $r=\infty$, where they have in common the electron configuration $5p_{\text{I}}{}^5\cdot 1s_{\text{H}}$.

Let us turn now to the finer details of the states corresponding to $5p_{\text{Xe}}{}^56s_{\text{Xe}}$ for $r=0$, to Q for $r>0$, and to $5p_{\text{I}}{}^5$ for $r=\infty$. For $r=0$ we have Jj coupling between $5p^5$ and $6s$, giving four states with $J=2$, 1, 0 and 1, respectively (corresponding to ${}^3P_{2,1,0}$ and ${}^1P$ of ordinary L, S coupling). For $r>0$ we at first come upon the "close-nuclei" form[8] of case c coupling (quantum numbers J and Ω). At r values large enough so that molecularization is able to break down this coupling, we have Ω-s coupling, in which we have state Q with five sublevels. Ω-s coupling may be expected to continue until, at relatively large r values, the separate-atom or "far-nuclei" type of case c coupling sets in (cf. Section 3).

The proper correlations of all the various substates at all stages can be worked out,[8] and are indicated in Fig. 1, except for $Q\ {}^3\Pi_2$ and $Q\ {}^3\Pi_{0^-}$. The latter both come from the level with $J=2$ at $r=0$, and go on dissociation into $\text{H}+\text{I}({}^2P_{3/2})$.

The foregoing discussion is applicable also, after making obvious changes, to the other molecules HX. These should differ only quantitatively from HI, the main changes being in the relative polarity and ionicness, and in the positions, of the several states. Roughly estimated $U(r)$ curves for states N and V of all the molecules HX have been given by Pauling.[7] According to the latter's work, the N and V states become about equally polar and ionic in HF, while in all the other HX, N is predominantly atomic and V predominantly ionic. However, V should probably always be less polar than N according to the theorem of I, Section 6.

In the series HI, HBr, HCl?, HF, the absorption wave-lengths corresponding to $Q\leftarrow N$ steadily decrease. In view of the pronounced tendency toward united-atom conditions shown in HI, the increase in the interval between N and Q in going from HI to HF can be understood in terms of the increase in the corresponding interval np^6 to np^5 $(n+1)s$ in the respective united atoms. It may be pointed out here also that the transitions $Q\leftarrow N$ in HX are much farther in the ultraviolet than the corresponding transitions in X_2, where the states Q are so low as in part to have minima in their $U(r)$ curves. This difference, and also the probable greater intensity of $Q\ {}^3\Pi_1\leftarrow N$ and $Q\ {}^1\Pi\leftarrow N$ and lesser intensity of $Q_0\leftarrow N$ in HX (in other words, the lesser applicability of postulates 2 and 3 of Section 4 to HX than to X_2 and XY) may well be connected with the closer approach to united-atom conditions in HX than in X_2.

As for states T and V, although we have no direct experimental data, the results on HCl^+ and HBr^+ noted above in connection with the discussion of the construction of Fig. 1 indicate that the heights of T and V above Q do not change much from HI to HBr to HCl, at least for r near r_e of state N. In view of the spectroscopic evidence mentioned above showing the increasing height of level Q above N as we go from HI to HF, we may then conclude, for r near r_e of N, that T and V also rise increasingly high above N in going from HI to HBr to HCl and, probably, to HF. According to date of Goodeve and Taylor on HI and HBr, even the height *above* $H+X(^2P_{1\frac{1}{2}})$ of level Q increases somewhat from HI to HBr, in spite of the increasing depth of the minimum of N below $\mathrm{H}+\mathrm{X}(^2P_{1\frac{1}{2}})$. If all this is correct, levels T and V, for $r=r_e$ of N, go increasingly high above the energy of $\mathrm{H}+\mathrm{X}(^2P_{1\frac{1}{2}})$ as we go from HI to HF. In the case of T, this conclusion is in complete agreement with what the Heitler-London theory would predict.

In the case of V, it is contrary to the behavior of the curves shown by Pauling, according to whom state V (both for its own r_e and for r_e of state N) should go progressively lower, relatively to the energy of $\mathrm{H}+\mathrm{X}(^2P_{1\frac{1}{2}})$, as one goes from HI to HF. Thus, although for HI, Pauling's V curve agrees closely with that shown here in Fig. 1, his V curve for HF is very much lower than would be obtained if the analogue of Fig. 1 for HF were constructed according to the methods here used. Experimentally, it is certain that the V curve of HF is at least 2 ev higher than Pauling's curve, since HF gas is transparent down to at least λ1950,[11] whereas according to Pauling's V and N curves, $V \leftarrow N$ absorption would be expected to begin near λ2750. According to estimates by the procedure here used, $V \leftarrow N$ absorption might be expected to lie in the neighborhood of roughly λ700 or λ800, i.e., near the first absorption lines of the neon atom (cf. HI, where $V \leftarrow N$ according to Fig. 1 should occur at wave-lengths approximately the same as for the transitions $5p^56s \leftarrow 5p^6$ in xenon).

The very high energy above N predicted for V according to the present procedure is based on the assumption that the structure of HF can be well approximated (for r near r_e of N) using united-atom or, better, molecular orbitals. As we have seen, the observed heights of the levels Q in HI and HBr, supported by the trend of the (incomplete) evidence for HCl and HF, tend to bear out this assumption. If the assumption is correct, level V should be above T, and both should be considerably above Q (just how much, in HF, could be better estimated if the HF^+ spectrum were known). A slightly different possibility is that the position of T may be about as just indicated, but that V may be lower due to its ionic character. This would be possible if the influence of the separated-atom atomic orbital approximation ($\mathrm{H}^+\mathrm{F}^-$) is still sufficiently pronounced, near $r=r_e$ of state N, to take precedence over the molecular or united-atom orbital approximation. In this connection, comparison may be made with a similar situation in LiH, where it is likely (cf. II, p. 1038, last complete paragraph) that the energy of state V, near $r=r_e$ of N, is near or perhaps even slightly lower than that of T, whereas for the corresponding united-atom (Be), V must be about 2.5 ev above T. Evidently, therefore, it is not impossible for V, due to its ionic tendencies, to come lower than one would expect using molecular orbitals, and even perhaps to come below T for a moderate range of r values (in this connection, cf. also the V state of AgI as shown in Fig. 2). Still, in view of the evidence for the goodness (better than in LiH) of the molecular orbital approximation in HX (of which HF should be the best case), it seems improbable that state V can lie, at worst, *much* below T in HF. Hence it appears probable that V actually lies very high in energy in HF, contrary to Pauling's curves.

6. The Molecules AgX; also CuX, AuX

The observed spectrum of each of the molecules AgCl, AgBr and AgI consists of a single band system, found both in absorption and emission (0,0 band at 3.90, 3.88, 3.84 ev, respectively), together with some continuous absorption mostly in the same spectral region.[5, 6] The bands appear to be single-headed, which would be in harmony with a $^1\Sigma^+ \leftrightarrow {}^1\Sigma^+$ type of transition. According to a private communication from Professor W. G. Brown, AgF also has a similar system of absorption bands at about λ2800, i.e., about 4.4 ev, followed by a gap and a continuum; the observed bands appear to form a sequence.

Let us call the upper electronic level of the observed bands B, the bands then being $B \leftrightarrow N$. The data on state B show a rapidly converging set of vibrational levels for each AgX, so that the energy of dissociation D can apparently be reliably estimated. The resulting D values according to Brice[6] are 0.31, 0.21, and 0.10 ev for AgCl, AgBr and AgI, respectively.

At the dissociation point of B, the total energy is found, using chemical D values (3.1, 2.6, 2.04 ev) for state N, to exceed the energy of unexcited $Ag+X$ by the amounts $E=1.1$, 1.5 and 1.9 ev for AgCl, AgBr and AgI, respectively. If we assume that the X atom is in the $^2P_{1/2}$ instead of the $^2P_{3/2}$ state on dissociation, E is reduced by 0.11, 0.45, 0.94 ev for Cl, Br, I, respectively, becoming about 1 ev for all three AgX. The assumption of an error of 1 ev in the chemical D values would dispose of this, but that would make the chemical D values unreasonably large; besides, Terenin's work[6, 13b] on AgI gives strong support to the accepted chemical D value there. On the other hand, the quantities E are certainly too small to be explained by assuming dissociation from state B to give any higher excited state of X or of Ag. For the lowest known excited state of Ag is the $d^{10}5p$ at 3.65 ev, while the as yet unknown d^95s^2, ^2D cannot be much lower than this, and is probably higher;[14] and the lowest state of I above the p^5, ^2P is p^46s, $^4P_{2\frac{1}{2}}$ at 6.74 ev.

One is driven to conclude, in disagreement with Brice's supposition of dissociation into $Ag(d^9s^2)$ plus $X(p^5)$, that the $U(r)$ curve of the B state must rise slightly with increasing r from its minimum to a maximum, then must drop again strongly to dissociate into $Ag(d^{10}s)+X(p^5,\ ^2P_{3/2}$ or $^2P_{1/2})$: cf. Fig. 2, where dissociation giving $^2P_{1/2}$ of X is assumed (for the reasons, see below). Although this type of behavior is unfamiliar in diatomic molecules, it is theoretically perfectly possible, and examples of more or less similar cases have already been found experimentally by Brown in ICl and IBr,[15] and by Hulthén and Rydberg in AlH.[16] It will now be shown that such behavior is not unreasonable in AgX if we identify state B as a resultant of the mutual interaction of three zero-approximation states of which two are the predicted states Q_0 and V.

The near ultraviolet spectra of AgX, like those of HX, might be expected to involve transitions $Q\leftarrow N$. In addition $V\leftarrow N$ might be expected as in MH. In HX, as we have seen, level V must be high up, because of the high energy of H^++X^- above $H+X$, so that $V\leftarrow N$ should be below $\lambda2000$. With AgX, however, Ag^++X^- is so low (cf. Table III of I) that V should come lower than in HX, although the larger size of Ag^+ as compared with H^+ acts as a restraining influence. If one estimates the course of the pure Ag^+X^- hypothetical $U(r)$ curve using Eq. (5) of I, taking A from Table III of I and β and n from crystal structure data, one finds that its calculated minimum comes below the energy of $Ag+X$. [The course of the pure Ag^+I^- curve for the case $\beta=0$ (pure Coulomb attraction) is shown by the dotted curve in Fig. 2.]

The situation may then be compared with that in MH (cf. II). In LiH, using Eq. (5) with crystal-structure values of β and n, the calculated minimum of the pure Li^+H^- curve came about 3.2 ev below the energy of $Li+H$; our analysis of the actual N and V states of LiH showed, however, that the minimum of the pure Li^+H^- curve must really be much less low, most likely only about 1.2 ev below the energy of $Li+H$. This error of about two ev in the minimum of the Li^+H^- curve calculated using crystal-structure data to get β and n is presumably related to the high polarizability of the H^- ion. In the case of the alkali halides MX, similar calculations of the energy of dissociation of the normal MX molecule, assuming it to be M^+X^-, agree rather closely with the experimental values. In the molecules AgX, it seems likely that we have cases somewhat intermediate between MH and MX in regard to the use of Eq. (5) with β and n from crystal structure data. Thus the calculated minima of the pure Ag^+X^- curves as here calculated may reasonably be expected to be perhaps 1 ev too low, so that these minima would very likely lie actually somewhat above the energy of $Ag+X$. Thus the pure Ag^+X^- curve would probably lie well above the pure $Ag\cdot X$, $^1\Sigma^+$ curve, and the molecules AgX be less polar than MH.

Nevertheless it is reasonable to suppose that the hypothetical pure Ag^+X^- and $Ag\cdot X$ curves

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[13b] Terenin's work gives a threshold value for the production of Ag (^2P) from AgI by photodissociation. This corresponds to an upper limit of 2.17 ev for D of AgI.

[14] Cf. H. A. Blair, Phys. Rev. **36**, 1531 (1930); also A. G. Shenstone, Phys. Rev. **31**, 317 (1928).

[15] W. G. Brown, Phys. Rev. **40**, 529 (1932); **42**, 355 (1932). Cf. also the $U(r)$ curve calculated for He_2^{++} by L. Pauling (cf. Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Co., 1935)); this He_2^{++} molecule is, however, of a type not likely to be met in band spectra.

[16] E. Hulthén and R. Rydberg, Nature **131**, 470 (1933).

come close enough together to interact strongly, as in MH, to give two new curves, the lower being that of the N state, the upper that of the V state. The N state would then be partially polar, for moderate r values, but less so than in MH. Qualitatively, the observed chemical D values for the N states of AgX are considerably larger than would be predicted from the additivity rule for homopolar bond energies (cf. II), using a reasonable estimate for D for Ag_2; and, following Pauling, we may take this difference as evidence that the bond in AgX is not nearly pure homopolar, but that strong interaction of the hypothetical pure homopolar $Ag \cdot X$ with the hypothetical pure ionic Ag^+X^- curve has occurred. [To be sure, the homopolar additivity rule fails in MH (cf. II) and apparently in MX, but the failure is in that the homopolar D values, i.e., the predicted values for the homopolar $M \cdot H$ or $M \cdot X$ curves, are too *small*, not too large. A similar failure here would only *strengthen* the indicated intensity in AgX of interaction between the pure Ag^+X^- and $Ag \cdot X$ curves.]

The interaction between the pure Ag^+X^- and $Ag \cdot X$ curves to give the actual N and V curves should, according to the foregoing, push up the V curve, especially at the smaller r values, very considerably above the position of the pure Ag^+X^- curve. One might then be inclined to identify the observed B state with the V state. This, however, is hardly possible in view of the form of the V, i.e., the Ag^+X^-, curve at large r values. Even at $r = 4.5$A in AgI (cf. Fig. 2), where the Ag^+I^- curve can hardly depart much from a pure Coulomb attraction curve, its energy has already descended well below that of the minimum of the B state. At smaller (but probably still rather large) r values, its energy must reach a minimum, and then probably should rise rather steeply due to the combined effects of the β/r^n term in Eq. (5) and the interaction with $Ag \cdot I$. No reason is apparent, in the discussion thus far, why the Ag^+I^- V curve should descend again to a second minimum at small r, as would be necessary if it were to be identified with the B state.

We have, however, not yet taken into account the predicted states Q. According to the method of molecular orbitals (cf. I, Table I and elsewhere), states N, Q, T, V have the electron configurations

$$N\colon \cdots\sigma^2\pi^4,\ {}^1\Sigma^+;\ Q,\ \cdots\sigma^2\pi^3\sigma^*,\ {}^{3,\,1}\Pi;\qquad T,\ V\colon \cdots\sigma\pi^4\sigma^*,\ {}^{3,\,1}\Sigma^+. \tag{3}$$

Furthermore it is expected that, as in other known cases (e.g. HX, X_2, XY), the order of binding is σ, π, σ^* so that N should be lowest, Q next, T and V highest. In other words, Q would be expected to lie below V and T, for r values comparable with r_e of state N.

We may then ask whether perhaps state B is Q_0, state V then being higher in energy and as yet experimentally unknown. If so, the occurrence of the elevated minimum in the B curve might perhaps be accounted for by a strong interaction of the V curve on the Q_0 curve. In investigating this idea, let us first consider how Q_0 and V should behave at large r values. As in other analogous cases (cf., e.g., HI) the Q_0 curve should tend on dissociation to give unexcited Ag plus $I(p^5,\ {}^2P_{1/2})$. Now it is important to note that if the Ag^+I^- V curve follows the Coulomb law fairly closely down to 4.3A, as we should expect, it should tend to cross the Q_0 curve at about this r value. If such crossing takes place, the V curve should descend to a minimum somewhat below the Q_0 curve, then should rise steeply as already suggested in a preceding paragraph, recrossing the Q_0 curve at smaller r values, in order that V may be above Q_0 at r values near r_e of N as demanded by our previous discussion of Eq. (3). Actually, it appears probable that both these crossings are avoided, so that two new curves result which do not cross. The full line curves in Fig. 2 are drawn in accordance with this idea. Of the two new curves resulting from the interaction of the original Q_0 and V curves, the lower one should have the characteristics[16a] of Q_0 for r values greater than about 4.3A, of V for a range of smaller r values, and finally of Q_0 again for still smaller r values. The upper of the two curves will be nearly pure V Ag^+I^- for $r > 4.3$A, nearly Q_0 for $r < 4.3$A for a while, and nearly pure V again for small r values.

Because of their complicated origin as resultants of two zero-approximation curves which cross and recross, both the actual curves should

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[16a] Really, for such large r values, we shall have not Q_0 but a case c 0^+ state corresponding to a mixture of Q_0 and N.

be somewhat irregular in form. The lower of the two curves might perhaps have a broad shallow minimum at large r values, but no reason is evident why it should have a second shallow minimum at small r values so as to permit it to be identified with the observed B curve. Such a second shallow minimum could occur only if the interaction between the zero-approximation V and Q_0 curves increased steadily and rather rapidly in intensity at moderate to small r values, but there appears to be no theoretical reason to expect such a behavior.

We are thus driven to examine the possibility that the B minimum belongs to a state which is primarily neither V nor Q_0. It appears at once that this possibility is very reasonable. Consider the states of AgI which should be derived from

$$\mathrm{Ag}: \cdots 4d\sigma 4d\pi^4 4d\delta^4 5s^2 \text{ plus I } \cdots 5p\sigma 5p\pi^4.$$

There should be a ${}^1\Sigma^+$ and a ${}^3\Sigma^+$ state, analogous to the N and T states. The ${}^1\Sigma^+$ state should show much stronger homopolar binding than would the Ag·I ${}^1\Sigma^+$ derived from unexcited Ag$(\cdots 4d^{10}5s)$ plus I, since the $4d\sigma$ of Ag is more suitable in form and energy than the $5s$ of Ag to give strong binding with $5p\sigma$ of iodine. A reasonable estimate of the binding energy would be about 2 ev. The actual binding energy, however, would be expected more or less to exceed this, because of polarity (influence of $\mathrm{Ag^+I^-}$ states) and probably also because of effects of interaction with a rather weakly bound ${}^1\Sigma^+$ state derived from Ag$(d^{10}p)$ plus I (see next paragraph).

The exact position of the d^9s^2 state above the $d^{10}s$ normal state of Ag is not known, but it is probably not far above the lowest known excited state $d^{10}p$ at 3.65 ev. An estimate of about 4 ev for the energy of excitation of the d^9s^2 state appears not unreasonable. [There should, of course, be a ${}^1\Sigma^+$ state derived from Ag$(d^{10}p)$+I, but this should have a much smaller dissociation energy than that from Ag(d^9s^2) plus I, because of much less favorable energy and form of $5p\sigma$ than of $4d\sigma$ of Ag for interaction with $5p\sigma$ of I. Hence, even though for $r=\infty$ this ${}^1\Sigma^+$ state derived from Ag$(d^{10}p)$ may be somewhat lower in energy than that from Ag(d^9s^2), for smaller r values the latter should most probably be decidedly the lower.]

Now it is a rather remarkable fact that in *all* the molecules AgX (cf. first paragraph of this section), the minimum of the B state is just about 4 ev above that of the N state. This would be explained if in each case the B state is essentially the ${}^1\Sigma^+$ state derived from d^9s^2 of Ag plus p^5 of X, and if also the energy of dissociation D of the B state into d^9s^2 of Ag plus p^5, ${}^2P_{1\frac{1}{2}}$ of I is approximately equal in each AgX to the D of the N state into unexcited Ag+X. The second condition appears entirely reasonable, as will now be shown. The D of state N is, as we have seen, surely considerably in excess of the homopolar D of normal Ag·X, due to strong polarity in the molecule. The homopolar D of the Ag·X state derived from Ag(d^9s^2) should be very considerably larger than the homopolar D of normal Ag·X. Considering, however, the effects of polarity and possible other influences in the two cases, it is more than merely plausible that the *actual* D of state N into unexcited Ag+X may be nearly equal, for all X, to that of state B into Ag(d^9s^2) plus X. Thus the supposition that state B, for r values near its minimum, is essentially the ${}^1\Sigma^+$ state derived from Ag(d^9s^2) plus I appears to be strongly indicated.

It remains now to explain why the potential energy curve of state B does not keep on rising until dissociation takes place into Ag$(d^9s^2, {}^2D_{2\frac{1}{2}})$ plus I$(p^5, {}^2P_{1\frac{1}{2}})$, but instead rises to a maximum and then descends to give unexcited Ag. The explanation is at hand if we observe that a B state curve going up to Ag(d^9s^2)+I would necessarily cross, at relatively small r values, the Q_0 and V curves discussed in preceding paragraphs. It is entirely reasonable to suppose that fairly strong interaction would take place near each of the attempted crossing points, so that the three curves would be replaced by three new curves somewhat like the three curves shown in Fig. 2. The lowest of the three would then correspond to the observed B curve, with its minimum and maximum. According to Fig. 2, this curve might have a second minimum at large r values; this, however, would not readily be detected in the spectrum. The wave function of this curve would have nearly B character for small r values, would acquire a strong flavor of Q_0 with some of V near its maximum, would take on mostly V character at larger r values, and finally would have case c 0^+ character (mixed Q_0 and N) at large r values.

An explanation which involves such a state of affairs may seem unduly complicated to readers who believe in using simple theories as far as possible. In the writer's opinion, however, the complexity is unavoidably inherent in the nature of the case in hand, so that probably every attempt at simplification would merely destroy all hope of real explanation.

The second lowest curve resulting from the interaction of the zero-approximation V, Q_0, and B curves is very likely a curve without a minimum, as shown in Fig. 2. Further investigation of the AgX spectra may throw further light on the actual forms of the curves which are shown, needless to say very tentatively, in Fig. 2. Data on the intensities of the transition $B \leftarrow N$ in the several AgX might also be useful in testing the present explanation of the B level.

It will be noted that, in our attempt to find analogous low energy levels and spectra in H_2, MH, HX, AgX and MX, we have been forced in the case of AgX to conclude that the lowest known excited electronic level and the known spectrum of AgX are *not* analogous to those of the other molecules. This lack of analogy we have traced to the d electrons in the outer part of the Ag atom, not present in the other cases. In the spectra of CuX and AuX, the effects of the d electrons should be much more conspicuous, since in Cu and Au, the d^9s^2 configuration is only about 1 ev above the normal $d^{10}s$ configuration, as compared with about 4 ev in Ag. This expectation is in accord with the observed spectra, which are quite different from those of AgX. In CuX, numerous band systems and low excited electronic levels (some showing evidence of predissociation) are known. In AuX, two low excited levels are known. An attempt to explain these various low levels in CuX and AuX would be of considerable interest. The present work on AgX should be helpful in preparing the way for this.

Returning to AgX, we have now to explain how it can be that, apparently, no transitions $Q \leftarrow N$ and $V \leftarrow N$ have been observed. Our analysis has shown rather definitely that the B state of AgX (for $r = r_e$ of state N) cannot be either Q_0 or V but must be *below* both of these (cf. Fig. 2). If this is correct, $V \leftarrow N$ and $Q_0 \leftarrow N$ should both be farther in the ultraviolet than $B \leftarrow N$, in a region not yet investigated; further, $Q_0 \leftarrow N$ should probably be represented only by a continuous absorption. Here it is important to note that the absorption work hitherto done on AgX extends only to about λ2500, not far beyond the region of the observed $B \leftarrow N$ bands. Extension of the spectrum toward shorter wavelengths should be important in working out the questions raised here.

Finally, we have to consider $Q\ {}^3\Pi_1 \leftarrow N$ and $Q\ {}^1\Pi \leftarrow N$. Assuming that the coupling (for r near r_e of state N) is approximately of Ω-s type for the Q states of AgX, the $Q\ {}^1\Pi$ level should be close to the Q_0, and the $Q\ {}^3\Pi_1$ somewhat lower (e.g., about 0.6 ev lower than the ${}^1\Pi$ in AgI). The ${}^1\Pi$ and ${}^3\Pi_1$ curves for AgI have been drawn in accordance with these specifications in Fig. 2. If Fig. 2 is essentially correct, the transitions $Q\ {}^1\Pi \leftarrow N$ and $Q\ {}^3\Pi_1 \leftarrow N$, like $Q_0 \leftarrow N$, and like the corresponding transitions in HX and MX (cf. Figs. 1, 3), should be represented only by continuous spectra.

Presumably the observed continua associated with the transitions $B \leftarrow N$ may, at least to some small extent, be attributable to $Q\ {}^3\Pi_1 \leftarrow N$. The transition $Q\ {}^1\Pi \leftarrow N$, along with $Q_0 \leftarrow N$, should lie considerably farther in the ultraviolet in the case of AgI, and both may so far have escaped detection for this reason (see above). In the case of AgCl, $Q\ {}^3\Pi_1 \leftarrow N$ should be close to $Q\ {}^1\Pi \leftarrow N$ and $Q_0 \leftarrow N$, but all should be considerably farther in the ultraviolet than $B \leftarrow N$ according to our theory. Further, $Q\ {}^3\Pi_1 \leftarrow N$ and $Q\ {}^1\Pi \leftarrow N$, and perhaps even $Q_0 \leftarrow N$, may be weak in all AgX (cf. postulate (2) of Section 4). Comparing different AgX, $Q_0 \leftarrow N$ would probably be strongest in AgI.

The continuous absorption which overlies the bands $B \leftarrow N$, extending also toward longer wavelengths, can be adequately accounted for by transitions to curve B on its small r side higher than its maximum, and on its large r side below and outside the maximum. The continuous absorption is most easily obtained in AgI, as one would expect since the height of the maximum of the B state is lowest there. Continuous absorption is obtained in AgCl only by strong heating.[6] This can be accounted for by the Franck-Condon principle. In AgCl it is found that the 0,0 band of $B \leftarrow N$ is the strongest,[6] indicating that r_e is not much different for B than for N. Thus, in the case of initially nonvibrating molecules, strong absorption transitions occur only to the stable region of the B curve near its minimum. On raising the temperature, the number of N molecules with strong vibrations increases, permitting transitions to other parts of the B curve, in particular to the parts outside its maximum.

In the case of AgI the strongest $B \leftarrow N$ band is no longer the (0,0), indicating that the difference between r_e of B and N is greater than for AgCl. The difference in ω_e values is also greater, as would be expected. In AgI, the maximum of the continuum[6] comes at a wave-length corresponding to 3.89 ev above $v=0$ of N, whereas the minimum of the B curve comes at 3.84 ev, its maximum at 3.94 ev. The agreement with our explanation is a reasonable one. Thus, empirically, it appears that the $^3\Pi_1 \leftarrow N$ continuum may indeed be very weak, as already suggested, since the observed continuum can be explained without assuming this transition at all.

Besides the main continuum in AgI, a much fainter one at longer wave-lengths and obtained only at very high temperatures, has been reported by Kuhn,[6] with a maximum corresponding to 3.08 ev. In view, however, of the high temperature used and the weakness of this continuum, it is probably safer to disregard it than to attempt to explain it, but with the recognition that it constitutes an unsolved problem.

In connection with the present explanation of the AgI spectrum in terms of Fig. 2, a further difficulty should be pointed out. According to Fig. 2, the $^3\Pi_1$ and $^1\Pi$ curves intersect the B curve near its minimum in such a way that one would expect predissociation to occur in the B state. While the existence of predissociation in AgI can hardly be either denied or affirmed on the basis of our present knowledge of the absorption spectrum, it must be admitted that the occurrence of the $B \rightarrow N$ bands of AgI in *emission* is rather strong evidence against the occurrence of predissociation. On the basis of this conclusion it seems probable that the $^3\Pi_1$ and $^1\Pi$ curves do not cross the B curve in the manner shown in Fig. 1. Raising the whole system of Q, T, and V curves, for r near r_e of N, would dispose of the predissociation difficulty and would be entirely consistent with the observed spectrum. The amounts by which the curves would have to be raised in order to avoid crossing of B near its minimum by $^3\Pi_1$ or $^1\Pi$ would, however, be rather considerable (see Fig. 2), and it is rather difficult to believe that these curves could be so high. On the other hand (considering also, especially, the evidence from AgBr and AgCl), the absence of pronounced absorption at longer wave-lengths than $B \leftarrow N$ makes it hardly tenable that the Q curves lie *below* the B curve. In the cases of AgBr and AgCl, the predissociation difficulty should be less troublesome than in AgI, since the several curves should be closer together. In any case, it is obvious that the present Fig. 2 does not represent a final complete solution of the problem of the low AgX energy levels and spectra; but it seems reasonable to believe that it represents progress in the right direction.

In concluding this section, the r_e and ω_e data on the B states of AgX deserve discussion. No direct experimental data on r_e are available, to be sure, but from the application of the Franck-Condon principle to the observed vibrational intensities (see above), it can be concluded that for AgCl, r_e is nearly the same for state B as for state N, while in AgI, r_e is somewhat, but not very much, greater for B than for N. On the other hand, ω_e is considerably less for state B than for state N, and the relative difference increases markedly from AgCl ($\omega_e=343$ for N, 281 for B) to AgI ($\omega_e=206$ for N, 131 for B). It is likely that in all AgX, but especially AgI, the ω_e's of state B are smaller than the usual rule, $r_e^2\omega_e$ or $r_e^3\omega_e=$constant for different states of a molecule, would predict.

It is of interest that a similar situation appears to exist in the $B\ ^1\Pi$ state of AlH where, although r_e is the same as for state N, ω_e is apparently relatively much smaller.[16] Less extreme examples are found in the normal states of HgH and analogous molecules; here, as in AlH, the phenomenon of abnormally small ω_e for given r_e is connected with, and probably a result of, an unusually small dissociation energy. The AgX case is similar, except for the large drop in energy with increasing r after the maximum of the potential energy curve is passed. In each case, the small r_e corresponds to the normal behavior of a stable molecular state with large dissociation energy, but the relatively small ω_e and the small actual dissociation energy, or the occurrence of a maximum in the curve, correspond to a rapid change in the character of the wave function with increasing r. Such behavior may be explained as a result of the strong interaction of two (or more) zero-approximation curves.[16b] In the case of AgX, the observed behavior is in good agreement with our explanation of the B state. In particular, the small r_e agrees with our supposition that the wave function near r_e is approximately that of a stable AgX with d-valent silver.

7. Molecules MX

Both emission and absorption spectra of MX are known.[3, 17] Most characteristic is the continuous ultraviolet absorption, which begins with two rather narrow regions of absorption, the first corresponding to dissociation into $M+X(^2P_{3/2})$, the second into $M+X(^2P_{1/2})$. The interval between the two maxima agrees approximately with the interval $^2P_{1/2}-{}^2P_{3/2}$ of X. Thus in the iodides the interval is reported as 0.98 ev in NaI, RbI and CsI, as compared with 0.94 ev for the I atom. In the bromides, intervals of about 0.4 ev are reported, as compared with 0.46 ev for the Br atom. Recently Levi[17] has reported an interval of 0.11 ev for NaCl and KCl, as compared with 0.11 ev for the Cl atom. Very little has been done with the fluorides.

This and further evidence indicate[3, 17] that the $U(r)$ curves of the upper levels involved in the continuous absorption all run in nearly horizontally[18] from $r=\infty$. The curves have only slight minima at large r, then begin to rise slowly. The energy of repulsion at $r=r_e$ of N varies only slightly in the several MX molecules for which data exist, from about 0.5 ev (RbI, CsI, KI) to about 0.8 ev (NaCl). [The determination of these repulsion energies is based on the positions of the absorption spectrum maxima combined with the dissociation energy D of the state N. The latter is rather accurately known in most cases from chemical data, supplemented in some cases by reliable determinations based on the ultraviolet spectra themselves, or on fluorescence, or both.[19]]

Besides the two continuum maxima just noted, further maxima are found farther in the ultraviolet. They are explainable by assuming a $U(r)$ curve for each excited state of $M+X$ [e.g., $M(ns, {}^2S)$ or $M(np, {}^2P)$ or $M((n+1)p, {}^2P)$ or $M((n-1)d, {}^2D)$, plus $X(^2P_{3/2})$ or $X(^2P_{1/2})$], *all these $U(r)$ curves running nearly parallel.*[17] That is, the continua maxima are spaced very nearly the same as the known levels of $M+X$ at $r=\infty$; this has been studied most thoroughly for CsI.[17]

In the electrically excited emission spectra of MX, also in chemiluminescence, a pseudo-band structure is found which is explainable by transitions from the large r regions of the upper $U(r)$ curves to the outer limb of the $U(r)$ curve of state N. Similar pseudo-bands are also found in absorption when the temperature is raised so that many molecules are in high quantum vibrational levels of state N. Analysis of such data (see Sommermeyer, and for the most complete results, especially Levi, Dissertation[17]) indicate that the $U(r)$ curves connected with $M+X(^2P_{3/2})$ and $M+X(^2P_{1/2})$ have very shallow minima at large r. Levi further concludes that the pseudo-bands for $M+X(^2P_{3/2})$,—or in one or two cases perhaps for $M+X(^2P_{1/2})$,—involve *two* shallow minima at different r values, hence at least two $U(r)$ curves from which strong transitions to state N occur. The observed continuum maximum for $M+X(^2P_{3/2})$,—or $M+X(^2P_{1/2})$,—is further identified by Levi as associated with one of the two $U(r)$ curves indicated by the pseudo-bands. Thus there appears to be spectroscopic evidence for at least three $U(r)$ curves derived from $M+X(^2P_{3/2})$ plus $M+X(^2P_{1/2})$. Theoretically (cf. Section 3) there should be five curves from $M+X(^2P_{3/2})$ and three from $M+X(^2P_{1/2})$, but spectroscopic transitions to two of the former and to one of the latter are forbidden; as for transitions to the

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[16b] For further discussion of this problem, cf. R. S. Mulliken, J. Phys. Chem., January (1937): from Princeton Symposium on Molecular Structure.

[17] E. v. Angerer and L. A. Müller, Physik Zeits. **26**, 643 (1925); L. A. Müller, Ann. d. Physik **82**, 39 (1927); A. Terenin, Zeits. f. Physik **37**, 98 (1926); V. Kondratjew, Zeits. f. Physik **39**, 191 (1926); A. Butkow and A. Terenin, Zeits. f. Physik **49**, 865 (1928); A. Visser, Physica **9**, 115 (1929); K. Sommermeyer, Zeits. f. Physik **56**, 548 (1929); H. Kuhn, Zeits. f. Physik **63**, 458 (1930); H. D. Schmitt-Ott, Zeits. f. Physik **69**, 724 (1931). H. Beutler and H. Levi, Zeits. f. Elektrochem. **38**, 589 (1932); H. Levi, *Dissertation* (Berlin, 1934). For a good review of most of this work, cf. W. Finkelnburg, Physik. Zeits. **34**, 539–541 (1933).

[18] P. K. Sen-Gupta, Zeits. f. Physik **88**, 647 (1934), discussing HX, MX, etc., points out relations between breadths and separations of the maxima, and steepness of $U(r)$ curves: e.g. in MBr, the $U(r)$ curve from $M+Br$ $(^2P_{3/2})$ is apparently a little steeper than that from $M+Br$ $(^2P_{1/2})$.

[19] H. Beutler and H. Levi, Zeits. f. physik. Chemie **B24**, 263 (1934).

rest of the curves, it is possible that some might be relatively weak.

The natural and probably correct conclusion which has been drawn from all this information is that two atoms M+X, in normal or in low excited states, come together without appreciable valence forces, so that the course of the $U(r)$ curves is governed by small van der Waals forces at large r and by the usual closed shell and Coulomb repulsive forces at small r; in short, that the excited MX molecules involved in the ultraviolet spectra behave like mere pairs of atoms. Or in other words, the coupling apparently approaches the ideal case *c* separate-atom type (cf. Section 3).

Considering now just the two maxima of continuous absorption corresponding to $\mathrm{M}+\mathrm{X}(^2P_{3/2,\,1/2})$, we may ask what relation they have to the expected states Q, T and V and to the expected transitions $Q(^3\Pi_1, {}^1\Pi)\leftarrow N$, $Q_0(^3\Pi_{0^+})\leftarrow N$, and $V(^1\Sigma^+)\leftarrow N$. In the first place, we notice that state N no longer has a $U(r)$ curve running down from two unexcited atoms $\mathrm{A}+\mathrm{X}(^2P_{3/2})$ as in other molecules AX, but now comes from $\mathrm{M}^+ + \mathrm{X}^-$. This change permits state V now to be correlated with $\mathrm{A}+\mathrm{X}(^2P)$ instead of with $\mathrm{A}^+ + \mathrm{X}^-$ as in our previous cases. In short, N and V have exchanged behavior as regards dissociation.

As we have seen in Section 3, the states Q, T and V are replaced for case *c* coupling by a corresponding set of states $\Omega=2$, 1, 0^-, 0^+, 1 derived from $\mathrm{M}+\mathrm{X}(^2P_{3/2})$ and forming a narrow bundle, together with a second narrow bundle of states $\Omega=0^+$, 0^-, 1 from $\mathrm{M}+\mathrm{X}(^2P_{1/2})$. The wave functions of the three states $\Omega=1$ should be mixtures of those of the Q states $^3\Pi_1$ and $^1\Pi$ and of the $\Omega=1$ component of T, $^3\Sigma^+$; those of the two 0^- states should be nearly 50, 50 mixtures of those of $Q\ {}^3\Pi_{0^-}$ and $T(^3\Sigma^+)_{0^-}$; those of the two 0^+ states should be nearly 50, 50 mixtures of those of $V\ {}^1\Sigma^+$ and $Q\ {}^3\Pi_{0^+}$. The selection rules allow transitions from $N\ {}^1\Sigma^+$ to the three $\Omega=1$ and to the two $\Omega=0^+$ levels. Since the three $\Omega=1$ wave functions all contain a $^1\Pi$ component, one expects transitions to all three to occur with comparable intensity, the sum of all these corresponding to the intensity one would have for $Q\ {}^1\Pi\leftarrow N\ {}^1\Sigma^+$ if one had had ordinary case *a* or *b* coupling. Similarly, transitions to the two 0^+ levels should be of roughly equal intensity, dividing between them the intensity which $V\ {}^1\Sigma^+\leftarrow N\ {}^1\Sigma^+$ would have had in case *b*, since each 0^+ level contains a $V\ {}^1\Sigma^+$ component. What the intensities of the transitions to the $\Omega=1$ states would be as compared with those to the 0^+ states is less clear.

If we adapt the postulates at the end of Section 4 to the situation, we conclude that strong transitions definitely should occur to the two 0^+ levels, the one derived from $\mathrm{X}(^2P_{3/2})$, the other from $\mathrm{X}(^2P_{1/2})$. This is in rough agreement with what is observed, if we ascribe the two continua essentially to $0^+\leftarrow N$ transitions. In addition, there should be transitions to the three $\Omega=1$ levels. If these should be weak, their superposition on two strong $0^+\leftarrow N$ continua would scarcely be noticed. Even if they are fairly strong, they need not much affect the appearance of the continuous spectrum, provided the several Ω levels derived from $\mathrm{M}+\mathrm{X}(^2P_{3/2})$ lie close together, and those from $\mathrm{M}+\mathrm{X}(^2P_{1/2})$ again close together. The evidence from Levi's analysis of the pseudo-bands indicates that transitions of appreciable intensity occur to at least two $U(r)$ curves derived from $\mathrm{M}+\mathrm{X}(^2P_{3/2})$. Assuming that one of these is to the 0^+ state, the others (theoretically there must be *two* others, though only one was definitely detected by Levi's analysis) must be to $\Omega=1$ states. Thus it seems likely that transitions to 0^+ and 1 states may be of comparable intensity. Theoretically, from a consideration of the probable forms of the wave functions, it appears likely that transitions to the 0^+ states should be the stronger.

We may next inquire whether, and if so how, the case *c* character of the excited electronic states of MX can be understood in terms of electron configuration theory. Especially, one wonders why case *c* states should occur replacing the V and T states; one would be inclined to expect that the usual Heitler-London valence attraction between $\mathrm{M}(\cdots ns,\ ^2S)$ and $\mathrm{X}(\cdots np\sigma np\pi^4)$ would give a fairly stable homopolar V state of the type M·X, $^1\Sigma^+$ and a rather strongly repulsive T state of type M·X, $^3\Sigma^+$. According to the "additivity" rule for homopolar bond energies,[20] one might expect M·X, $^1\Sigma^+$ to have a D about equal to the average of those of

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[20] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

M_2 and X_2, i.e., about 1 or 2 ev (cf., Pauling's curves of this type,[7] which are, however, too deep as compared with the later developed additivity rule). Further, it may be asked why the Q states should not lie well below the V and T states, as we have in Section 5 shown to be necessary in HX on the ground of a consideration of the molecular orbital approximation and of the spectra of HX^+.

We shall seek a reasonable answer to these questions by considering first the molecular orbital approximation for MX, then the Heitler-London-Slater-Pauling approximation, and then looking for a way of reconciling the two approximations with each other and with the spectroscopic evidence for case *c* coupling. Using molecular orbitals, the electron configurations of states N, Q, V and T of MX would be as follows (cf. Table I and Eq. (3) of I):

$$N:\ \cdots\sigma^2\pi^4;\quad Q:\ \cdots\sigma^2\pi^3\sigma^*;\quad V,T:\ \cdots\sigma\pi^4\sigma^*.$$

As discussed following Eq. (3) of I, the orbital σ would be pure $np\sigma$ of atom X if MX in its normal state N were pure heteropolar M^+X^-, while σ^* would then be pure $ns\sigma$ of M; π is nearly pure $np\pi$ of X in any case, but can best be classified as a molecular orbital for the present purpose.

Suppose we consider the electronic structure of MX from the standpoint of the *Aufbauprinzip*, starting, say, with $(MX)^{++}$, and assuming the nuclei always held fixed at a distance r equal to r_e of state N of MX. Here, in the lowest electronic state, the structure may be described as M^+X^+, with the M^+ outer shell complete, but with X^+ containing two electrons less than a closed shell np^6. If now one more electron is added, giving $(MX)^+$, the lowest states by far are clearly the two states

$$\cdots\sigma^2\pi^3,\ {}^2\Pi\quad\text{and}\quad\cdots\sigma\pi^4,\ {}^2\Sigma^+,$$

in which the σ and π orbitals are essentially $np\sigma$ and $np\pi$ of X. The Hartree field in which these molecular orbitals exist is of the general type M^+X^+, but the lowest energy solutions of the Schrödinger equation for this field are, clearly, very nearly atomic orbitals of X, since these have much lower energy, for $r=\infty$, than the lowest unfilled orbitals of M. The two above states ${}^2\Pi$ and ${}^2\Sigma^+$ are then both approximately of character M^+X. Due to the polarizing action of the M^+ on the X, however, the molecular orbitals σ and π are not quite pure $np\sigma_X$ and $np\pi_X$, but are a little distorted and give a little M–X homopolar bonding, especially the σ, which should have slightly lower energy than the π. The ${}^2\Pi$ state should then be the normal state of $(MX)^+$, with the ${}^2\Sigma^+$ just a little higher in energy. [By way of comparison, it may be recalled that in $(HX)^+$ the energy difference between the ${}^2\Pi$ normal and the ${}^2\Sigma^+$ excited state is observed to be about 3.5 ev (cf. Section 5).]

If now the last electron is added, the state of lowest energy is certainly that with configuration $\sigma^2\pi^4$, in which the p^6 shell of X is completed. This addition of an electron to the X atom tends to make it X^- and give a molecule of character M^+X^-. The σ and π orbitals, however, are now in a Hartree field of the general type M^+X and are less firmly bound than in M^+X itself, and so are much more strongly polarized by the M^+. Their departure from pure $np\sigma_X$ and $np\pi_X$ should then be much greater than in the ${}^2\Sigma^+$ and ${}^2\Pi$ states of $(MX)^+$. As a result, σ should give probably an appreciable amount of M–X homopolar bonding.

Suppose now, however, that the last electron added to $(MX)^+$ to form MX is added not to the lowest energy orbital available, but to the orbital of next lowest energy. Since $(MX)^+$ in either of its two states of lowest energy is essentially of the character M^+X with only a little mutual interaction between the M^+ and the X, the available molecular orbitals are essentially atomic orbitals of M or of X^-. Since the term value is probably nearly zero for all excited orbitals of X^-, the electron will find its resting place preferably in an M atom orbital; practically any such orbital, aside from those which are already occupied in M^+, will give a lower energy than if the electron settled in an excited X^- orbital. We are thus led, by the application of the method of molecular orbitals, to excited states of MX in which an electron is added to either of the two low $(MX)^+$ states ${}^2\Pi$ and ${}^2\Sigma^+$ in a molecular orbital which is very nearly a pure M atom orbital. Automatically, these excited states turn out to be of the character MX or M′X, i.e., an association of a normal or excited (M′) atom with a normal X atom, the last electron being in an orbital of nearly pure M character, and the next to last electrons in orbitals of nearly pure X character. The distortion of the σ and π orbitals as compared with pure $np\sigma_X$ and $np\pi_X$ should be even less in these excited states of MX than in the low states of $(MX)^+$, since we now have a neutral M atom instead of an M^+ as distorting agent.

The lowest excited states of MX should be those in which the last added electron is in an orbital nearly identical with $ms\sigma$ of M, the valence orbital of M. This slightly distorted $ms\sigma_M$ is to be identified with σ^* of Eq. (3) of I. As lowest excited states of MX we then get from the $^2\Pi$ of M^+X the states

$$\cdots\sigma^2\pi^3\sigma^*,\ ^{1,\,3}\Pi\ (Q\text{ states});$$

and from the $^2\Sigma^+$ of M^+X the states

$$\cdots\sigma\pi^4\sigma^*,\ ^{1,\,3}\Sigma^+\ (V\text{ and }T\text{ states}).$$

In all of these states, besides inner electrons, we have essentially five unshared, nonbonding, np electrons of X and one unshared, nonbonding, ns electron of M.

In the preceding, we have tacitly neglected the effects of spin-orbit coupling in the X atom. Actually, if there is no appreciable valence coupling between the atoms, this becomes important. We referred above to $\sigma^2\pi^3$, $^2\Pi$ and $\sigma\pi^4$, $^2\Sigma^+$ of $(MX)^+$ and to $\sigma^2\pi^3\sigma^*$, $^{1,\,3}\Pi$ and $\sigma\pi^4\sigma^*$, $^{1,\,3}\Sigma^+$ of MX. Really, however, if the σ and π are nearly pure X atom $p\sigma$ and $p\pi$ orbitals, little affected by the M atom, the division into σ and π becomes merely hypothetical, and instead of $\sigma^2\pi^3$, $^2\Pi$ and $\sigma\pi^4$, $^2\Sigma^+$ of X we expect p^5, $^2P_{3/2}$ and p^5, $^2P_{1/2}$ of X. In M^+X, the $^2P_{3/2}$ should be slightly split into two case c levels with $\Omega=3/2$ and $1/2$, while the $^2P_{1/2}$ should remain as a single level, with $\Omega=1/2$. In excited neutral MX, we then expect essentially $(\cdots p^5,\ ^2P_{3/2})_X\cdot(\cdots s)_M$ giving case c levels $\Omega=2,\ 1,\ 1,\ 0^+,\ 0^-$ and $(\cdots p^5,\ ^2P_{1/2})_X\cdot(\cdots s)_M$ giving levels $\Omega=1,\ 0^-,\ 0^+$. Thus the weakness of the valence coupling between M and X in excited MX, or between M^+ and X in $(MX)^+$, indicated by our molecular orbital approach, leads automatically for these states to atomic orbitals with case c coupling. At the same time it causes states Q, V and T to be nearly equal in energy, and the resulting case c coupling then mixes up various components of these states in the way we have seen.

How, now, does the situation look from the H.L.S.P. point of view? In first approximation we get for the normal state the structure $M^+X^-(\cdots\sigma_X{}^2\pi_X{}^4)$, and for the low excited states $M\cdot X(\cdots ms_M\cdot\cdots\sigma_X{}^2\pi_X{}^3$ and $\cdots ms_M\cdot\cdots\sigma_X\pi_X{}^4)$, essentially the same as by the method of molecular orbitals. The states $\cdots ms_M\cdot\cdots\sigma_X{}^2\pi_X{}^3$, $^{1,\,3}\Pi$ are the Q states, and according to the H.L. method we expect no valence attraction here between the M and the X.

In the case of the states $\cdots ms_M\cdot\cdots\sigma_X\pi_X{}^4$, $^{1,\,3}\Sigma^+$ we are at first inclined to expect a fairly strong valence interaction between s_M and σ_X, giving a rather stable state V, $^1\Sigma^+$ and a rather strongly repulsive state T, $^3\Sigma^+$. As already noted above, the homopolar bond additivity rule would predict a D of 1 or 2 ev for the V, $^1\Sigma^+$ state. This rule is, however, empirical, and in view of its failure in the molecules MH (cf. II), it may reasonably be expected here also that D for $s_M\cdot\sigma_X\pi_X{}^4$, $^1\Sigma^+$ should fall much below the value predicted by the rule. The valence attraction in $^1\Sigma^+$ (or repulsion in $^3\Sigma^+$) would then be very weak, and the whole group of excited states should then give place to the corresponding case c states, in harmony with the results of the molecular orbital approach and with the empirical spectroscopic evidence.

Before accepting this, let us see whether the failure of the additivity rule in MH and MX is theoretically reasonable. If we consider the (perhaps hypothetical) *pure homopolar state* A·A, A·B, B·B of each of three molecules A_2, AB and B_2, it is not unreasonable that the additivity rule should hold (D of A·B equal to average of D values of A·A and B·B) provided the valence orbital of atom A is fairly equal to that of B in size and density. This condition is fulfilled in most of the cases discussed by Pauling in connection with the additivity rule. If, however, the valence orbitals of A and B are very unequal, then it appears that the overlapping and the exchange integrals might be much less favorable for the interaction of a valence electron of A with one of B than for the valence electrons of two A atoms, or of two B atoms. From this standpoint, failure of the additivity rule should be more complete (i.e. D smaller compared with the additivity rule value) in MX than in MH; and in MH we have strong semiempirical evidence that the rule fails badly. [This is apparently contradicted by Heitler-London theoretical calculations on MH, neglecting inner shells, but these are hardly reliable, and on the whole the semiempirical evidence appears to carry much more weight: cf. II. In this connection, theoretical calculations on M·X would of course be of interest, but the effort of making them properly would seem likely to be excessive.] On the whole, thoroughgoing failure of the additivity rule in M·X, leaving only weak valence forces between M and X, and allowing case *c* coupling to become dominant, gives an explanation of the excited states of MX which may be said to have a fairly high probability of being essentially correct. Granting this, there still remain of course many details to be further investigated and explained, such as the intensities and forms of the various continua and bands, which show interesting features differing from one molecule to another.

In the preceding paragraphs it has been tacitly assumed that all molecules MX may be treated alike with respect to the question of the dominance of case *c* coupling over valence forces. This assumption now requires consideration. While dominance of case *c* coupling appears reasonably possible for MI and MBr, where the internal spin-orbit couplings in the halogen atoms are relatively large, it would seem to be more doubtful for MCl and especially MF, unless the valence interactions become extraordinarily small in the latter. In favor of the latter possibility, however, is the trend of the argument in the last preceding paragraph, since maximum inequality between the valence orbitals of M and F occurs in MF. In any case, dominance of weak valence over weak case *c* coupling in MF should not much affect the positions of any but the V and T levels (and these probably not greatly), nor should it much affect the appearance of the spectrum. Careful study of the as yet little known MF spectra might, however, show something of interest.

Before concluding this section, one further matter connected with the separated-atom or Heitler-London approach must be considered and if possible disposed of. This is the question whether there ought not to be strong interaction between the two first approximation states $M^+X^-(\cdots\sigma_X^2\pi_X^4,\ {}^1\Sigma^+)$ and $M\cdot X(\cdots s_M\cdot\sigma_X\pi_X^4,\ {}^1\Sigma^+)$. In MH, AgX, and other cases, we have assumed, and found evidence for, strong interaction between the corresponding first approximation states. Certainly in MX there must be some interaction of this sort.

May it be that the homopolar additivity rule really *does* hold after all for $M\cdot X(s_M\cdot\sigma_X\pi_X^4)$, but that the resulting ${}^1\Sigma^+$ state then interacts strongly with the M^+X^- state, pushing the latter down, and itself getting pushed up, enough to make it *appear* that the additivity rule fails, and to allow case *c* to take hold? [Case *c* will take hold of this $V\,{}^1\Sigma^+$ state if *for any reason* it gets sufficiently close to the $Q\,{}^3\Pi_0{}^+$ state.[21]] Under the circumstances just outlined, the T state $M\cdot X(s_M\cdot\sigma_X\pi_X^4,\ {}^3\Sigma^+)$ would be strongly repulsive, and would probably escape from case *c*; this possibility, it must be admitted, is not contradicted by the available spectroscopic evidence, since transitions to such a non-case-*c* T state from the N state should be weak.

The possibility that the situation just sketched may exist in MX cannot easily be denied on the basis of the empirical data, since it does not differ sufficiently from that obtained assuming thoroughgoing failure of the additivity rule. More probably correct, however, in the writer's opinion, is a situation compounded as follows: (A) the additivity rule fails badly, and there is only very weak valence coupling in *all* states M·X, so that states V and T, as well as Q and also other higher excited states, become approximately of case *c* type; (B) the pure heteropolar unpolarized M^+X^- character of the first approximation normal state wave function is modified not by strong interaction just with the first approximation $s_M\cdot\sigma_X\pi_X^4$, $V\,{}^1\Sigma^+$ state, but by the sum total of weaker interactions with the first approximation wave functions of this and a whole series of other M·X (and other) excited states. The possibility that condition (B) exists in MX is favored, as compared with MH, AgX or HX, by

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[21] Cf. J. H. Van Vleck, Phys. Rev. **40**, 568 (1932).

the fact that the pure M^+X^- state is well below the whole set of states $M\cdot X$ and $M'\cdot X$ in energy, while in the other molecules the A^+B^- state is close to or even in the midst of the $A\cdot B$ states.

It seems possible that the wave function of state N of MX, resulting from the operation of condition (B), may be describable more or less roughly as "classically polarized" in contradistinction to the "valence polarized" condition that would exist if the pure M^+X^- function were modified mainly just by strong interaction with the valence bond state $s_M\cdot\sigma_X\pi_X{}^4$, $^1\Sigma^+$. In classically polarized M^+X^-, the whole p^6 shell of X would be shifted relative to the X nucleus and inner electrons (the inner shells are relatively slightly affected), while in valence polarized M^+X^-, just the orbitals of the two σ electrons would be shifted, and also distorted. In a molecule like HF or AgX, state N might be described as (very strongly) valence polarized A^+X^-. If state N of MX is approximately "classically polarized" M^+X^-, the polarization is shared by the σ and π orbitals and therefore need not be so very great for either. In other words, the σ orbital of Eq. (3) of I is in this case nearly pure $np\sigma_X$. Possibly of significance in the present connection is the fact that the Born equation (Eq. (5) of I) with crystal-structure values of β and n gives values, for the energy of dissociation D of state N of MX into ions M^++X^-, which are close to the actual D values, while for other molecules, the D's calculated in this way are much larger than the actual (cf. II in regard to LiH, Section 6 above for AgX).

The electronic structures of the normal and excited states of MX which result, as just discussed, starting from the H.L.S.P. viewpoint and using the conditions (A) and (B) above, are in excellent agreement with those reached in earlier paragraphs using the molecular orbital viewpoint.

In connection with state N of MX, it is worth noticing here that the dipole moments,[22] although not accurately known, are apparently at least half as large as would be expected for pure heteropolar M^+X^-. If as an approximation we assume that the reduction of the dipole moment to half is due to a "classically polarized" condition, then of the total polarization only one-sixth belongs to each of the electrons in the group $p\sigma^2p\pi^4$ which makes up p^6. To give the observed dipole moments, each of these six p electrons need be displaced only one-twelfth of the distance from X to M. This corresponds to only a small modification in the σ and π orbitals as compared with pure $np\sigma_X$ and $np\pi_X$ orbitals.[23]

In conclusion, the writer wishes to express his appreciation of the valuable help of Mr. H. J. Plumley in connection with the construction of the figures.

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[22] H. Scheffers, Physik. Zeits. **35**, 425 (1934); W. H. Rodebush, L. A. Murray, Jr. and M. E. Bixler, J. Chem. Phys. **4**, 372, 536 (1936); dipole moments of NaI, KCl, KI by molecular ray method.

[23] R. S. Mulliken, J. Chem. Phys. **3**, 584 (1935).