I. MICROWAVE SPECTROSCOPY

INTRODUCTORY PAPER:

QUADRUPOLE COUPLINGS, DIPOLE MOMENTS AND THE CHEMICAL BOND

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It is particularly fitting that a discussion of microwave and radio-frequency spectroscopy be conducted under the auspices of the Society which bears the name of Michael Faraday. Faraday's discoveries in electromagnetism led Maxwell to predict, and later Hertz to discover, radio waves. Faraday's experiments in electrolysis revealed the quantization of electric charge and the electrical aspects of matter which are responsible for the interaction of these radio waves with material particles. Faraday's ice-pail experiments presaged the invention of microwave cavities and wave-guide. It was Faraday's search for a common denominator for all physical manifestations which led him to his discoveries of basic relations between electricity and magnetism, between electricity and matter, between magnetism and light. One day in 1822 Faraday set out to find a relation between magnetism and light. Twenty-three years later, twenty-two years and some odd months after all ordinary men would have lost heart and quit, Faraday succeeded. Thus Faraday's work led to the development of the implements or tools of microwave and radio-frequency spectroscopy. His belief in the unity of physical reality gives philosophical purpose to this discussion. His patient persistence in his endeavours demonstrates the proper psychological attitude for those who would do the precise measurements and careful analysis of modern spectroscopy.

Considering the early discovery of radio waves, it is puzzling that their use for spectroscopy came so late. In 1946 both microwave and radio-frequency spectroscopy were just beginning, yet the radio waves of Faraday, Maxwell and Hertz were known and had been used in numerous practical applications for half a century. We " pure " scientists can take no pride in this. We can only point with pride to the rapid progress we made once we did start to tune in the atoms and molecules on our radios. Probably never before in the history of science has so much highly precise and diverse information about the structure and properties of matter been obtained in a comparable span of time by any other method as has been accumulated within the past decade from microwave and radio-frequency spectroscopy. If you doubt this statement, it may be that your senses have been dulled by the bang of the hydrogen bomb which occurred during the same period. By inserting the modifiers " highly precise and diverse ", I have sought to disqualify the great bulk of information obtained with X-rays and electron diffraction.

We in this Discussion are not concerned with the structure of the nucleus, and I shall not speak about the large amount of nuclear information which has been gained via radio waves. We are not concerned with astronomy, and I shall not tell how one microwave spectral line is unravelling the structure of our galaxy and informing us of the composition of interstellar space. I am not supposed to

tell you of the new knowledge of the solid state being gained from electron spin resonance and cyclotron resonance at microwave frequencies, nor of the invasion of biology by microwave spectroscopists. I was asked to give an introduction only to the microwave spectroscopy of gases. Even that is too much to introduce properly in a single speech. Hence, I shall attempt a proper introduction to only one aspect of the subject—that of nuclear quadrupole couplings—but I shall first call your attention to certain other aspects.
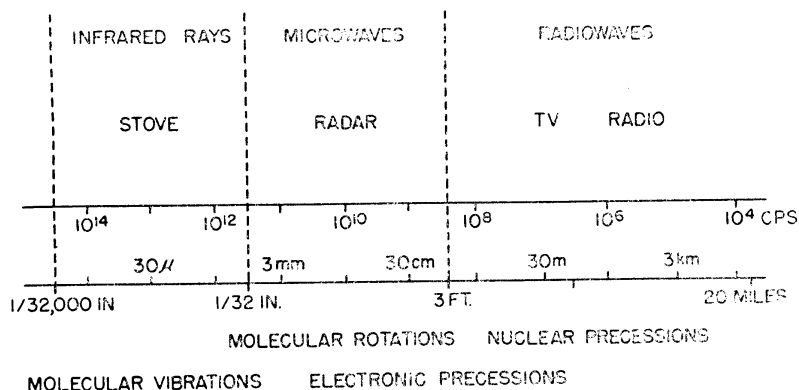

FIG. 1.—Spectral space of the microwave region.

The spectral space of the microwave region is indicated in fig. 1. With microwave electronic methods we at Duke have measured spectral lines down to 0·77 mm wavelength.[1] In Czerny's infra-red laboratory at Frankfort, Germany, an infra-red grating spectrometer has been used by Genzel and Eckhardt [2] to measure rotational lines up to 0·99 mm wavelength. The microwave and infra-red frontiers have thus overlapped. No virgin territory remains in the entire electromagnetic spectrum except at its boundless ends. The last territory to be explored, our last spectral reserve, is indeed a fertile one. Here molecular lines are strong and abundant—orders of magnitude more so than in the centimetre wave region —yet the high resolution and precise measuring methods of microwave electronics are still applicable (see fig. 2).
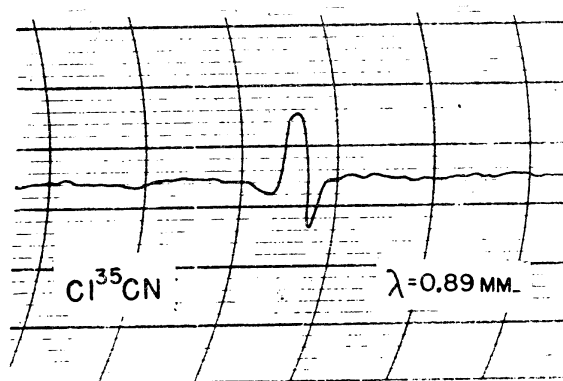

FIG. 2.—Microwave rotational line ($J = 27 \rightarrow 28$) of ClCN in sub-millimetre region $\lambda = 0.89\,\mu$. Measured frequency 334,219·5 Mc/s; line width, 0·4 Mc/s; cell volume 0·4 cm^3 (from Burrus and Gordy).[1]

Just as molecular vibrational frequencies fall in the infra-red region and nuclear precessional frequencies in the conventional radio region, rotational transitions of nearly all molecules fall in the microwave region. Most of the molecular information from microwave spectra has been obtained from rotational spectra— but not from simple, unperturbed rotational spectra. Superimposed on the

rotational motions of molecules are nuclear precessions and also molecular precession when an external magnetic or electric field is applied. The structure of rotational spectra arising from nuclear or external field interaction allows the microwave spectroscopist to obtain considerably more information about the molecule than he could obtain from an unsplit rotational line. The type of information obtainable from the rotational spectra alone, bond angles and bond lengths, is widely appreciated and needs no special attention in this introduction. Microwave structural evaluations are generally more accurate than those from other sources, and they are being accumulated at a rapid rate. The same applies to electric dipole moment determinations from the Stark effect of microwave rotational spectra. Resolvable Zeeman splitting of rotational lines of practically any molecule can be produced by fields of 5 to 20 kilogauss. Numerous gaseous free radicals should be detectable with microwave spectroscopy, and a few have been so detected. Molecular electric quadrupole moments and collision diameters can be ascertained from microwave line shape measurements. Prof. A. Kastler has pointed out to me that molecular twisting vibrational transitions of many large organic molecules in solids should be observable in the one-milli-metre-wave region.

The marriage * of microwave and optical spectroscopy has been brought about by ingenious proposals of Bitter [3] and of Kastler [4] whereby microwave or radio-frequency energy is used to change the distribution of the Zeeman levels of an optically excited substance so that observable light of a particular polarization is radiated. This is a development truly in the spirit of Faraday.

QUADRUPOLE COUPLINGS, DIPOLE MOMENTS AND THE CHEMICAL BOND

Because the information which nuclear quadrupole coupling can (or cannot) give about the chemical bond is not widely appreciated, I shall treat this subject in some detail. The manner in which these coupling constants are deduced from the hyperfine structure [5] of rotational spectra need not be described.

The coupling constant which is obtained directly from an analysis of the hyperfine structure of symmetrical molecules is eQq, in which e is the charge on the electron, Q is the electric quadrupole moment of the coupling nucleus, and q is the electric field gradient at the nucleus with reference to the charge-symmetric axis. From atomic beam measurements, Q is now accurately known for the halogens Cl, Br, and I, and for B. Whenever the coupling of one of these nuclei is measured in a molecule, the field gradient q is determined.

An electron i at a distance r_i from the nucleus gives rise to a potential, $V = e/r$ at the nucleus and a field gradient,

$$q_i = \left(\frac{\partial^2 V}{\partial z^2}\right)_i = \frac{\partial^2}{\partial z^2}\left(\frac{e}{r}\right)_i = \frac{e\,(3\cos^2\theta_i - 1)}{r_i^3}. \tag{1}$$

In the last form θ is the angle between r and the z axis. To obtain the contribution of the ith electron to the observed q, one must average the above quantity over the orbital of the electrons of the molecule. The total q can thus be expressed as

$$q = \sum_i \int \psi_i q_i \psi_i^* d\tau, \tag{2}$$

with the normalization,

$$\int \psi_i \psi_i^* d\tau = 1. \tag{3}$$

Eqn. (2) suggests at once how quadrupole coupling might give information about the electronic structure of a molecule: it links the measurable quantity, q, to the wave functions of the molecular electrons. It also reveals at the outset

* The marriage ceremony, I understand, was performed by Bitter and Brossel (*Physic. Rev.*, 1950, **79**, 775).

the difficulties facing anyone who would arrive at chemical bond information in this way. The difficulties are the same ones that always plague those who seek to solve the chemical bond problem in an elegant and exact manner. There are many more electrons in the molecule than there are observables, and we do not really know the correct ψ_i for any of them. We must make assumptions, some questionable, to apply our new datum. Nevertheless, we are proud of our number q. It is more accurately measured than are most other quantities around which assumptions are constructed.

We can ignore all electrons except those in the valence shell of the coupled atom, A. This represents a sweeping simplification of the problem, and yet it is not hard to justify, at least to the semi-practical man, namely, the chemical physicist. Electrons on other atoms are too far away and the inner-shell clouds of A have too much symmetry to make significant contributions to q_A. Our problem resolves to one of guessing what happens to the electronic cloud of its valence shell when the atom forms a chemical bond. I consider this an attractive way of putting the problem, for I know that there is no greater sport for the chemist or chemical physicist than that of guessing what happens when a chemical bond is formed. For a halogen atom which forms an orthodox single bond, the simplest first guess is that nothing much happens to any of the orbitals except the one which gets mixed up with an orbital of the neighbouring atom.

Let us suppose that the A-orbital in question is represented by the wave function, ψ_a, and the B-orbital with which it gets involved by ψ_b. By a popular convention we then express the new molecular orbital as the mixture,

$$\psi = a\psi_a + b\psi_b, \tag{4}$$

with the yet undetermined mixing coefficients a and b. We assume that the two electrons are in the bonding orbital represented by ψ and express their combined contribution to q_A by

$$(q_A)_{bond} = 2a^2\int\psi_a q_i\psi_a^*\,d\tau + 4ab\int\psi_a q_i\psi_b^*\,d\tau + 2b^2\int\psi_b q_i\psi_b^*\,d\tau. \tag{5}$$

The last term of eqn. (5) represents the contributions to q_A of electronic charge density in the atomic orbital of B, which, because of the inverse cube variation of q with r are negligible. The term next to the last, while larger than the last, is less than 1 % of the first term for halogens considered here. We, therefore, throw away both of the last terms and have left only

$$(q_A)_{bond} = 2a^2\int\psi_a q_i\psi_a^*\,d\tau, \tag{6}$$

which, except for the factor $2a^2$, is simply the contribution of a single electron in the atomic orbital ψ_a.

Let us first assume that ψ_a is a p orbital of A. The other p orbitals are then filled with unshared pairs and the d orbitals are empty. The total q_A can then be obtained most simply by treating it as arising from a p_z electron deficit of $(2 - 2a^2)$ electrons in an otherwise spherical cloud. The atomic coupling, on the other hand, arises from a deficit of exactly one p electron in an otherwise closed shell. Therefore, we can write

$$\text{molecular } q_{total} = (2 - 2a^2)(- 2) \text{ atomic } q_{total}, \tag{7}$$

in which the factor of -2 corrects for the difference in orbital orientation of the unbalanced p electron in the molecule and in the free atom. By multiplication of both sides of eqn. (7) by eQ it is found on rearrangement that

$$a^2 = 1 - (\rho_q/2), \tag{8}$$

where for future convenience we designate

$$\rho_q \equiv \left|\frac{\text{molecular } eQq}{2 \text{ atomic } eQq}\right|. \tag{9}$$

Let us see if the a^2 values thus obtained have any meaning.

We consider first the homopolar molecule for which $a = b$. For it, one obtains from the normalization of eqn. (4),

$$a^2 = \frac{1}{2(1 + S_{ab})}, \tag{10}$$

in which S_{ab} is the overlap integral $\int \psi_a \psi_b d\tau$. The measured couplings substituted in eqn. (8) gives $a^2 = 0.50$ for both Cl_2 and Br_2. These values with eqn. (10) indicate $S_{ab} = 0$. The overlap integral obtained with Mulliken's tables [6] indicates the very different values $S_{ab} = 0.34$ for Cl_2 and $S_{ab} = 0.31$ for Br_2, and hence the values $a^2 = 0.36$ and 0.38. The inconsistency can be removed by postulation of large amounts of s hybridization, 30 to 35 % for the atomic orbitals ψ_a, if one likes to postulate hybridization.

It is a little more cumbersome to handle, but if one employs the unnormalized Heitler-London wave function for the pure covalent bond,

$$\psi = c[\psi_a(1)\,\psi_b(2) + \psi_b(1)\psi_a(2)], \tag{11}$$

and follows through the evaluation of q_A in the same way by assuming pure p orbitals, one finds that

$$c^2 = 1 - (\rho_q/2), \tag{12}$$

which yields with the observed couplings, $c^2 = 0.50$ for Cl_2 and for Br_2. With the normalizing requirement of the Heitler-London function,

$$\int \psi \psi^* d\tau = c^2(2 + 2S_{ab}{}^2) = 1, \tag{13}$$

the couplings again require $S_{ab} = 0$. Mulliken's values of S_{ab} with eqn. (13) give $c^2 = 0.43$ and 0.46 for Cl_2 and Br_2. Because of the different expression for the normalization, a postulation of only 10 to 12 % s character for the atomic orbital ψ_a would this time make harmony. Nevertheless, it is fair to ask: if the l.c.a.o. molecular orbital approximation can be 35 % wrong here, may not the Heitler-London approximation be at least 12 % wrong?

The difficulties brought out in the above discussion originate principally, I think, from the following conditions. Because of inverse cube variation with r, the major part of the nuclear quadrupole interaction arises from the relatively small part of the valence orbitals which lies within the major lobes of the inner shells. Contrary to the implications of the usual normalizations, significant charge density is not lifted from regions near the nuclei to help form the cloud which I do not deny is piled up between the nuclei when the covalent bond is formed. The orbital overlap distortions occur mainly in the outer regions of the atoms where the nuclear coupling is insensitive to charge redistributions. Both the Heitler-London (H.-L.) and the l.c.a.o. molecular wave functions as conventionally normalized appear to over-emphasize distortions near the nucleus—the latter more than the former. For dealing with nuclear quadrupole coupling it appears permissible to ignore the overlap integral [7] and to normalize the wave functions by setting $S_{ab} = 0$. The normalization then gives a^2 or $c^2 = \frac{1}{2}$ for homopolar bonds, or $a^2 + b^2 = 1$ for polar ones. In treating dipole moments, bond energies, or other properties which are sensitive to charge redistributions in the outer parts of the atom, we cannot of course do this.[8]

The setting of $S_{ab} = 0$ seems to free the nuclear coupling from the chemical bond and thus to end our story. Actually, this is no more than one-third true. So far we have considered only pure covalent bonds (no ionic character) formed out of unhybridized atomic orbitals. Unlike orbital overlap, ionic character can decrease significantly the electron density of the bonding atomic orbital in regions close to one nucleus because this density is in effect transferred to a comparably low potential region near the other nucleus. Furthermore, a pure covalent

bond through scrambling (hybridization) of the atomic orbitals can alter the angular distribution of the electronic charge cloud near the nucleus and thus can influence the coupling without lifting charge density appreciably away from the nucleus, although some lifting of course accompanies the hybridization.

To examine the effects of bond orbital hybridization and ionic character let us go back to eqn. (6) and consider $a \neq b$, with

$$\psi_a = a_s\psi_s + a_p\psi_p + a_d\psi_d. \tag{14}$$

If cross-terms are neglected, eqn. (6) then becomes

$$(q_A)_{bond} = 2a^2\Big[a_s^2\int\psi_s q_i\psi_s^*\mathrm{d}\tau + a_p^2\int\psi_p q_i\psi_p^*\mathrm{d}\tau + a_d^2\int\psi_d q_i\psi_d^*\mathrm{d}\tau \Big]. \tag{15}$$

The first integral here is zero because the s electronic cloud is spherically symmetric. The second represents the contribution of the p electron already described. The third integral is small because the d orbital is non-penetrating. It is further reduced by the factor a_d^2 which should insure that its contribution to q_A in the halogens is less than 1 %. We, therefore, drop both the first and the last terms on the right and have left,

$$(q_A)_{bond} = 2a^2 a_p^2\int\psi_p q_i\psi_p^*\mathrm{d}\tau. \tag{16}$$

This expression gives only the contribution of the hybridized bonding orbital. To get the total q_A we must consider other orbitals, some of which will be counter-hybridized. We choose the p orbital involved to be the p_z. The counter-hybridized sp_z orbital will have a_s^2 amount of p character and will contain an unshared pair of electrons, while the counter hybridized $p_z d$ orbital will have a_d^2 amount of p_z character but will be empty. As before, the p_x and p_y orbitals contain unshared pairs. There will be a resultant p_z population of $2a^2a_p^2 + 2a_s^2$. The total q_A will arise from a p_z electron deficit of $(2 - 2a^2a_p^2 - 2a_s^2)$ in an otherwise spherical cloud. With the normalizations $a_s^2 + a_p^2 + a_d^2 = 1$ and $a^2 + b^2 = 1$, and with the representation,

$$\text{ionic character} = \beta = a^2 - b^2, \tag{17}$$

one obtains

$$\text{molecular } eQq = [1 - a_s^2 + a_d^2 - \beta(1 - a_s^2 - a_d^2)](- 2 \text{ atomic } eQq),$$

or

$$\beta(1 - a_s^2 - a_d^2) + a_s^2 - a_d^2 = 1 - \rho_q. \tag{18}$$

A more exact expression which contains an averaged correction for the changes in nuclear screening in the halogen is

$$\beta(1 + 0.13\rho_q - a_s^2 - a_d^2) + a_s^2 - a_d^2 = 1 - \rho_q. \tag{19}$$

In these equations a_s^2 represents the s character and a_d^2 the d character of the bond orbital of A. A negative sign of β corresponds to a positive charge on the coupling atom. Because we have set S_{ab} as zero, our designation of ionic character is equivalent in magnitude to ionic character as conventionally defined in terms of ionic-covalent resonance concepts.

The difficulty with eqn. (18) or (19) is that it contains three parameters and only one observable. A fortunate circumstance exists, however. If we revert to the homopolar molecules Cl_2 and Br_2, with their observed $\rho_q = 1.00$ and $\beta = 0$, we learn from eqn. (18) that either there is no hybridization or $a_s^2 = a_d^2$. If correction is made for the cross-bonding [9] in the macromolecule of crystalline I_2 as indicated by its asymmetry parameter, we learn similarly that for I_2, $a_s^2 = a_d^2$, to a very close approximation. Although we are compelled again to employ solid state data for the pure homopolar bonds, the ρ_q values for the gaseous state of the nearly homopolar molecule BrCl, indicates $a_s^2 \approx a_d^2$ for any reasonable value of β. Furthermore, a consistent interpretation of the Cl and I coupling

in ICl requires either no hybridization for either atom or nearly equal s and d hybridization. Now if we consider completely ionic molecules such as KCl or KBr for which $\beta = 1$ and $\rho_q = 0$ (observed), we find from eqn. (18) that $a_d^2 = 0$, and that possible effects of s hybridization drop out. In other words, the experimental evidence is that hybridization does not exist either in the pure covalent or in the pure ionic state X^+Hal^- unless it exists in such form as to have no observable effects on the coupling. Therefore we suspect that there is probably
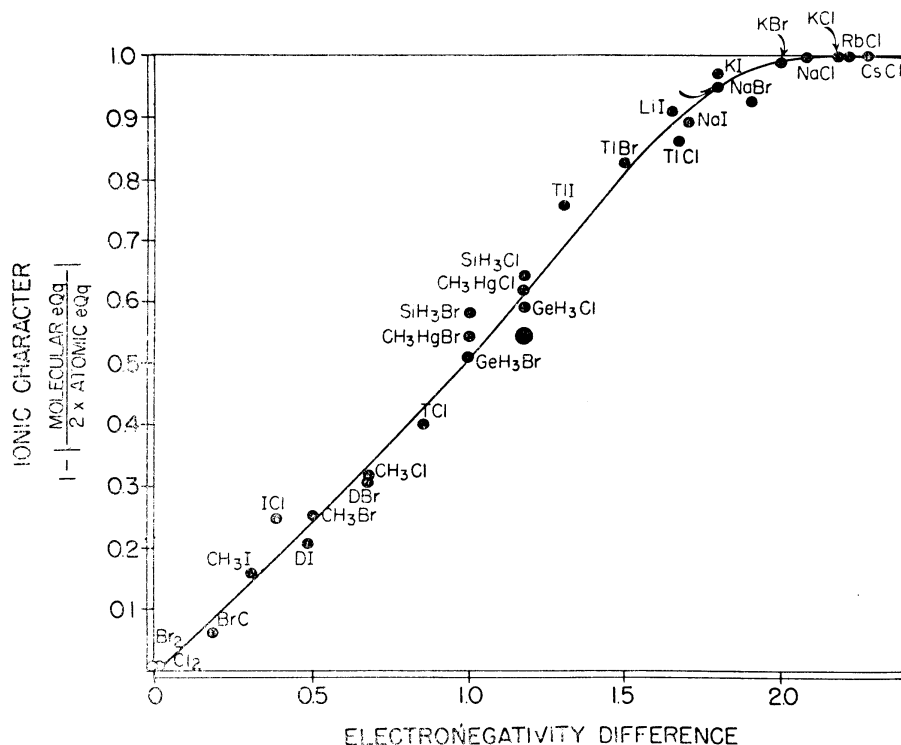

FIG. 3.—Plot of ionic character (as indicated by nuclear coupling) against electronegativity difference. The x values [16] for: H, 2·13; Li, 0·95; Tl, 1·3; Cl, 2·98 are from ref. (16). When rounded off to 2 figures, these coincide with Pauling's, except for Tl, for which Pauling gives no value. The value for CH_3 is from force constants (see table 3). Other values are from Pauling [12] except that Haissinsky's value (*J. Physique*, 1946, **7**, 7) of 2·6 for I is employed. The hydrogen halide couplings are from ref. (11); the Tl halide couplings from Mandel and Barrett (*Bull. Physic. Soc.*, 1955, p. 20); and the alkali halide couplings from Hornig *et al.* (*Physic. Rev.*, 1954, **96**, 621). The other couplings are listed in ref. (5).

little, if any, of the detectable kind in mixtures of the two. Later I shall state other reasons for suspecting this. With this evaluation of the constants from the neutral and negative end points, $a_s^2 = a_d^2 = 0$, eqn. (18) becomes

$$\beta = 1 - \rho_q, \qquad (20)$$

or more precisely,

$$\beta = (1 - \rho_q)/(1 + 0·13\rho_q). \qquad (21)$$

Eqn. (20) or (21) should give a rather good measure of the ionic character of the type which puts the negative pole on the coupling halogen. In the approximate considerations to follow, the screening effects of the negative charge will be neglected, since at most they cause only 0·03 charge in β. For a positive charge, the screening effects are more serious and must be considered. Eqn. (21) applies also for positively charged atoms when there is no hybridization; but for a large positive charge, hybridization effects may not be negligible.

The ionic characters obtained with eqn. (20) for a number of simple molecules are compared with the electronegativity difference of the bonded atoms in fig. 3 and 4. These plots indicate that the relation between ionic character and electronegativity difference is approximately but not exactly linear. Because of the inexactness of the best available electronegativities, one cannot quibble over the non-linearity except, of course, where the curve levels off at the top. It reveals that for electronegativity differences greater than two the bonds are purely ionic
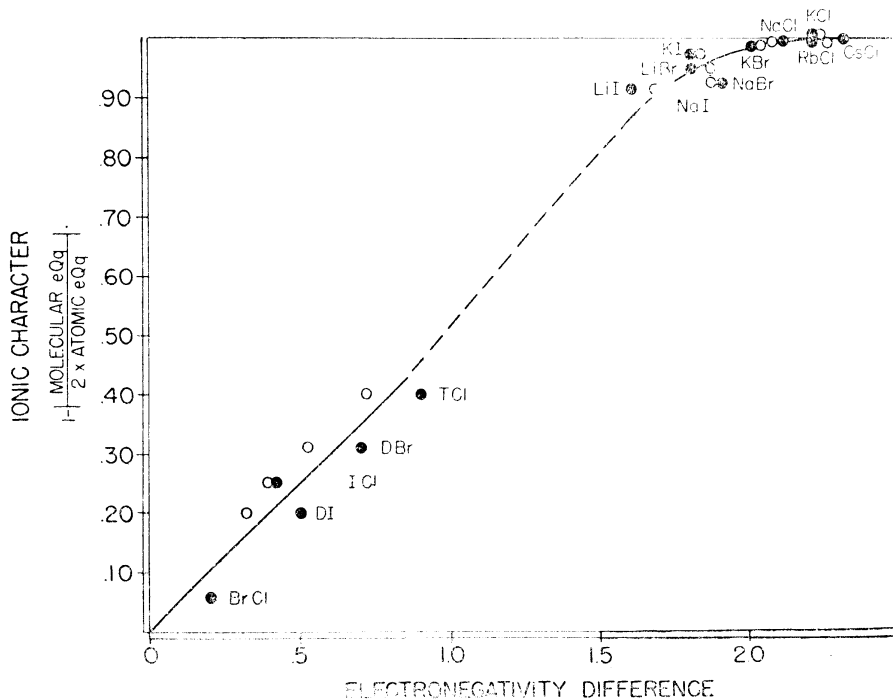

FIG. 4.—Plot of ionic character against electronegativity difference with Mulliken's scale (open circles) and with Pauling's scale (solid dots). The Mulliken scale for H and for the first and second row elements is that obtained by Skinner and Pritchard (*Trans. Faraday Soc.*, 1953, **49**, 1254). In both plots the Haissinsky value 2·6 for I is used. The only significant difference in the two scales is for H, 2·28 (M) and 2·1 (P).

and that a small electronegativity difference leads to significant ionic character. The convenient approximate rule,

$$\text{ionic character} = (|\,x_A - x_B\,|)/2 \text{ for } |\,x_A - x_B\,| < 2,\qquad(22)$$

for estimating ionic character derived earlier,[10, 7] from meagre coupling data is borne out by the more complete data now available. The plot of data on hundreds of polyatomic molecules, including molecules in the solid state shows a wider scattering of points about the same line if Pauling's electronegativity scale is used. This mass agreement occurs because Pauling's scale represents mean values chosen from a variety of molecules and because various deviating factors tend to balance in the aggregate. The π character, about 10 %, expected in the SiHal bonds,[5] if taken into account, would improve the agreement of fig. 3.

In contrast to the mass approach there is the discriminating approach which includes only those molecules for which the parameters involved are most accurately known. Fortunately, both lead to the same relation here. Fig. 4 shows the result of the discriminating approach. Even here there are two very respectable electronegativity scales, Pauling's and Mulliken's, which must be considered, but again the weighted average agrees with fig. 3.

The couplings of the hydrogen halides recently measured in the one-to-two millimetre wave region [11] are particularly significant for the above relation. It

was with the dipole moments of the hydrogen halides that Pauling [12] estimated the ionic character values which he used to obtain the first ionic character against electronegativity relation. Because he did not correct for the large overlap moment (then unknown) which in the hydrogen halides opposes the primary moment, it is understandable that his relation (see fig. 5) predicts much lower values for ionic character than the nuclear couplings and dipole moments now indicate.
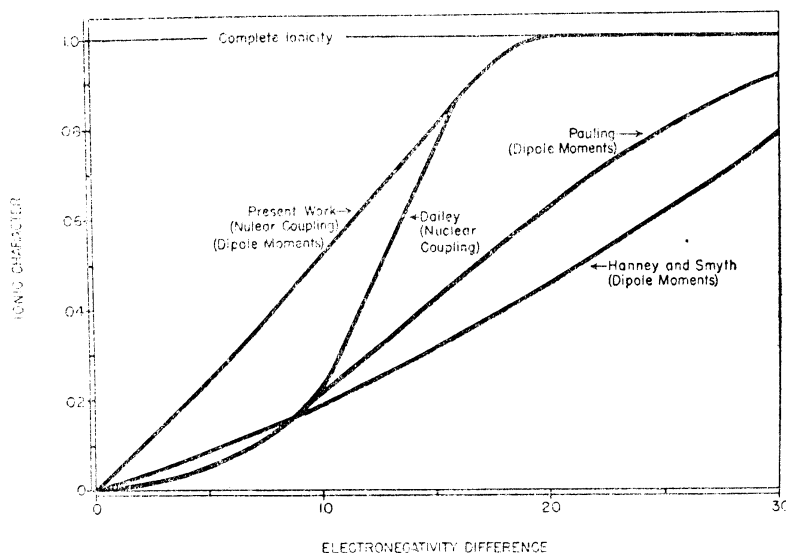

Fig. 5.—Comparison of various ionic character electronegativity relations. Pauling's relation is from ref. (12); Hannay and Smyth's from *J. Amer. Chem. Soc.*, 1946, **68**, 171; Dailey's from *J. Physic. Chem.*, 1953, **57**, 490. A relation similar to that of Dailey's is recommended by Townes.[26]

Although I consider the values from quadrupole coupling the more reliable, I shall attempt to calculate ionic character from the dipole moments of the hydrogen halides and alkaline halides just to show that there is not necessarily any disagreement between the two methods. According to modern concepts, the dipole moment can be expressed as the sum of four parts,

$$\mu = \mu_p + \mu_s + \mu_h + \mu_i. \tag{23}$$

The first term on the right is the primary moment which arises from ionic character; it is given by βed. This is the term which is of interest to us, but in order to find it from the observed moment we must evaluate the other terms. The second term on the right is the overlap moment, the significance of which was first recognized by Mulliken. It can be expressed [13] as

$$\mu_s = 4abeS_{ab}\, z_S \approx \frac{-2e\, S_{ab}}{1 + S_{ab}}\left(r - \frac{d}{2}\right), \tag{24}$$

where r is the covalent radius of the larger atom, and d is the internuclear distance. The third term represents the atomic hybridization moment of Coulson.[14] It is zero when there is no hybridization, as we shall here assume. The last term μ_i is the polarization or induced moment.

In the ionic or nearly ionic alkali halides we can neglect both μ_s and μ_h, and have only to evaluate μ_i. This we do in an elementary manner. Classically the polarization moment can be expressed

$$\mu_i = E_a\alpha_a + E_b\alpha_b, \tag{25}$$

where α_a and α_b are the polarizabilities of the ions A and B, and where E_a and E_b are the polarizing fields assumed to be uniform over the ions. The latter is,

of course, not exactly true in our case. To obtain an estimate of E_a, we assume it to arise from an effective charge on B, $\mu_{obs.}/d$, equal to its observed pole. Similarly, the field E_b is obtained from the effective pole on A. Quite simply, but only approximately,

$$\mu_i = \frac{\mu_{obs.}}{d^3}\,(\alpha_a + \alpha_b). \tag{26}$$

With eqn. (23) and (26) and with $\mu_h = 0$, $\mu_s = 0$ the ionic character is

$$\beta = \frac{\mu_{obs.}}{ed}\left(1 + \frac{\alpha_a + \alpha_b}{d^3}\right). \tag{27}$$

Eqn. (27) has been used to calculate ionic characters for the alkali halides, which are compared with those from nuclear coupling in table 1. If, instead of the effective pole, the full electronic charge is used with the classical method of Debye [15] to calculate μ_i, ionic characters greater than unity are obtained. Although we think we know that ionic characters greater than unity do not occur here, the results are still in agreement with the quadrupole coupling in that complete ionicity is indicated when $|\,x_A - x_B\,| > 2$.

TABLE 1.—PREDICTED IONIC CHARACTER

molecule	from dipole moment μ_p/ed	from Hal. coupling $1 - \rho_q$	from electronegativity $\|x_A - x_B\|2$
HCl	0·41	0·40	0·42
HBr	0·35	0·31	0·34
HI	0·18	0·21	0·23
LiBr	0·90	0·95	0·93
LiI	0·90	0·91	0·83
NaCl	0·97	1·00	1·00
KCl	1·01	1·00	1·00
KBr	0·97	0·99	1·00
KI	0·98	0·98	0·90
CsCl	0·99	1·00	1·00

In the hydrogen halides, where the proton is essentially embedded in the side of the halogen, it is very difficult to calculate the induced moment, but we know from geometrical reasoning that it will be much smaller than that given by eqn. (26) and therefore not very large. Although I do not know how he did it, Mulliken [13] calculated μ_i for HCl as 0·3 D. I have used this value with the μ_i ratios obtained from eqn. (26) to estimate the μ_i for HBr and HI given in table 2.

TABLE 2.—ESTIMATION OF IONIC CHARACTERS FROM DIPOLE MOMENTS

	μ_s (calc.)[a]	μ_i (calc.)	$\mu_h{}^a$	$\mu_{obs.}$	calc. $\mu_p = (\mu_{obs.} - \mu_s - \mu_i)$	ionic character μ_p/ed
HCl	− 1·14	− 0·3	0	1·08	2·52	0·41
HBr	− 1·38	− 0·2	0	0·80	2·38	0·35
HI	− 1·70	− 0·1	0	− 0·42[b]	1·38	0·18

[a] assumes pure p orbitals for halogen, pure s for H.
[b] The sign of μ_p is taken as positive, whereas the observed moment of HI is assumed to be in opposition and hence negative.

To calculate the overlap moment I have used eqn. (24) with Mulliken's [6] S_{ab} values for a pure p bonding orbital of the halogens. The primary moment used to estimate ionic character is then obtained by addition of these quantities to the observed moment, with $\mu_h = 0$, as shown in table 2. It is interesting that in HI the overlap moment is so large that the observed moment is in opposition to the primary moment, i.e. the negative pole is at the hydrogen end.

In addition to coupling evidence against it, dipole moment considerations do not favour hybridization when the ionic resonance puts the negative charge on the halogen. Suppose that a bond X-Hal of length 2 Å has 50 % ionic character, of the kind X^+Hal^-. There would then be a primary moment of 4·8 D, with the negative pole on A. This large primary moment would strongly tend to quench any sp atomic hybridization moment on A which would of necessity be in the same direction as the primary moment when the negative charge is on Hal. Furthermore, in the diatomic interhalogens, where the smaller atom is always the more electronegative, the overlap moment would be in the same direction as the primary moment and would assist in the quenching. Actually, in a molecule like ICl if there is 15 % s character or even 10 % in the Cl bond orbital and no hybridization in the I orbitals, an atomic hybridization moment of the order of 2 D would add to the primary and overlap moments to give a total of several Debye to be cancelled down to the observed moment of 0·54 D by the induced atomic moment, which here must be in opposition to the atomic hybridization moment. Also, this type of hybridization would increase the electronegativity of Cl but not of I and would hence increase the already too large moment still further. All these factors, on the other hand, favour hybridization on the positively charged atom; and both the quadrupole couplings and the dipole moments of the molecules FCl and FBr indicate that some hybridization may exist at the positive end, possibly as much as 10 %, if the bonds are normal single bonds, as they may not be.

No s character is in evidence for either the Br or Cl orbitals in BrCl, nor for either halogen of ICl. In BrCl the Br coupling indicates 10 % ionic character, and the Cl coupling indicates only 6 %. This disagreement is not serious, and is only made worse by postulation of s character on either halogen. Small amounts of d hybridization could clear up the discrepancy, which could also be caused by small errors in the coupling and estimated correction for screening. If we choose the average value of 8 % for the ionic character, the primary moment is $0·08 \times 2·14 \times 4·8 = 0·82$ D. The overlap moment for pure p orbitals is 0·17 D in the direction of μ_p, whereas the opposing induced moment is estimated from eqn. (26) to be 0·45 D. The total moment predicted in this way is 0·54 D, whereas the observed moment is 0·57 D. A similar but less certain analysis for FBr and FCl leaves a sizeable difference to be cancelled by π feed-back and possibly by a hybridization moment on the positive halogen. The ionic character of ICl predicted without hybridization by eqn. (21) with the Cl coupling is 23 % and with the I coupling is 24 %. This agreement is excellent. A postulation of s hybridization (without d) on either or both atoms would (as in BrCl) make the agreement worse, not better.

A consideration of the fact that more s charge would be lifted out of a given s hybridized orbital of A when $a^2 < b^2$ than when $a^2 > b^2$ might lead one to conclude that s hybridization in the halogens would occur at the negative but not at the positive pole. However, this is by no means the only consideration. Already atomic dipole effects have been mentioned as favouring hybridization on the positive pole. Other things being equal, it would seem reasonable that the type of hybridization would be favoured which would lower rather than raise the electronegativity difference of the bonded atoms. This appears to be borne out in FCl for which the bond energy with Pauling's method gives $(x_F - x_{Cl}) = 0·76$, whereas Mulliken's method for pure p orbitals gives $(x_F - x_{Cl}) = 0·90$. A little s character on Cl would clear up the discrepancy, whereas s character on F would only make it worse.

As a general rule, the dipole moment would tend to sustain the hybridization on the positive atom and to quench it on the negative atom. Probably never in a molecule is there hybridization of the type which would significantly increase an already large total moment. In such molecules as PF_3, AsF_3, $AsCl_3$ and $SbCl_3$ a large atomic hybridization moment on P, As, or Sb is in opposition to

the primary moment as well as the overlap moment. Note that in these molecules s hybridization occurs on the positively charged atom. In NF_3, where the overlap moment is negligible and the polarization moment small, the large primary moment of the NF bonds is almost cancelled by the comparably large atomic hybridization moment on N, to give the small observed moment of only 0·23 D. If the negatively charged F atoms had significant hybridization, this would not be true, and a large moment would be expected. In AsH_3 the primary moment is very small ($\Delta x = 0.1$), but there is a large overlap moment which opposes the comparably large hybridization moment of As so that the observed moment is only 0·16 D. In H_2S the overlap and primary moments are opposed but leave a resultant of approximately 0·6 D pointing in the same direction as the atomic hybridization of μ_s to give the observed moment of about 1 D. Like H_2S, H_2O and NH_3 are rather exceptional in that an atomic hybridization moment points in the direction of the resultant moment, but the large bond angle, short bond length, and opposing overlap moment keep down the resulting moment to reasonable size.

If the quadrupole coupling data are interpreted correctly here, then ionic character is a much more sensitive function of electronegativity difference than has been previously supposed (see fig. 5 for example). It follows that the moderate variations in electronegativity with chemical bonding state have much more influence on ionic character, and hence upon physical and chemical properties of molecules, than has been previously supposed. Furthermore, with the electronegativity quadrupole coupling relation shown in fig. 3 we can use nuclear quadrupole coupling of the halogens to evaluate effective electronegativities of atoms bonded in various chemical groups regardless of whether we admit nuclear coupling as measuring ionic character. The relation can be expressed approximately as

$$\frac{x_{Hal} - x_X}{2} = 1 - f_q. \tag{28}$$

where x_X is the effective electronegativity of the atom bonded to the coupling halogen. In using this relation one must always be sure that no significant double bond character exists in the bond. An application is made in table 3.

TABLE 3.—EFFECTIVE ELECTRONEGATIVITY OF C IN THE METHYL GROUP [a]

molecule	from force constant eqn. (30)[b]	from Hal eQq eqn. (28)
CH_3Cl	2·37	2·38
CH_3Br	2·34	2·30
CH_3I	2·28	2·29
	av. 2·33	av. 2·32

[a] When $x_{Cl} = 3.0$, $x_{Br} = 2.8$, and $x_1 = 2.6$.
[b] With force constants by Linnett (*J. Chem. Physics*, 1940, **8**, 91). Noether's force constants (*J. Chem. Physics*, 1942, **10**, 664) for CD_3Cl and CD_3Br yield the x values 2·38 and 2·39, respectively, for the methyl group.

When, as is most often the case, the π bond component in the double bond character is formed through donation of an unshared p pair by the coupling halogen, the unbalanced p_z charge is reduced and the coupling is lowered. If the amount of such π character is designated by γ_π then it is easily shown that the above relations become approximately

$$\beta_\sigma = 1 - \left(\frac{\gamma_\pi}{2}\right) - f_q = \frac{x_{Hal} - x_X}{2}, \tag{29}$$

in which β_σ represents the ionic character of the σ component. When the effective electronegativities are known, these relations can be used to estimate the ionic character of the σ component as well as the π character of the bond.

With the help of other relations to estimate effective electronegativities, I shall now apply eqn. (29) to certain types of bonds in polyatomic molecules. The force constant against electronegativity relation,[16]

$$k = 1.67(x_A x_B / d^2)^{3/4} + 0.30 \qquad (30)$$

with the force constants given by Herzberg [17] for C_2H_2, 5.92 and for C_2D_2, 5.99, and with the interatomic distance $d = 1.057$ Å, the electronegativity of the sp orbital of C is obtained as 2.7. A somewhat higher value is expected for the sp hybrid in XCN because of the effects of the electronegative N. From the decreased screening of C in the latter compound I have estimated the C in XCN as 0.1 higher, or 2.8. With eqn. (29) and these x values of carbon, I have estimated the π character of the C—Hal bond adjacent to triple bonds as given in table 4. As expected, the

TABLE 4.—DOUBLE BOND (π) CHARACTER AND IONIC CHARACTER PREDICTED FROM QUADRUPOLE COUPLINGS AND ELECTRONEGATIVITIES

mo ecule	coupling ratio for Hal ν_{q}(obs.)	π character of C Hal (%)	ionic character of σ component of C Hal[d] (β_σ)%	resultant ionic character of C Hal $(\beta_\sigma - \gamma_\pi)$%
ClCN	0.76[a]	28	10	− 18 (Hal.[+])[e]
HCCCl	0.73[b]	25	15	− 10
BrCN	0.89[a]	22	0	− 22
CH_3CCBr	0.84[c]	22	5	− 17
ICN	1.06[a]	8	− 10	− 18
CH_3CCl	0.98[c]	14	− 5	− 19

[a] Smith, Ring, Smith and Gordy, *Physic. Rev.*, 1948, **74**, 370. Townes, Holden and Merritt, *Physic. Rev.*, 1949, **74**, 1113.

[b] Westenberg, Goldstein and Wilson, *J. Chem. Physics*, 1949, **17**, 1319.

[c] Sheridan and Gordy, *J. Chem. Physics*, 1952, **20**, 735.

[d] Electronegativities employed are: 3.0 for Cl, 2.8 for Br, 2.6 for I, 2.7 for C≡C—, 2.8 for N≡C—.

[e] A minus sign for $(\beta_\sigma - \gamma_\pi)$ corresponds with a positive charge on the halogen.

π character decreases from Cl to I. In all cases it is in satisfactory agreement with that predicted from a consideration of bond lengths. Goldstein and Bragg [18] have shown that the asymmetry parameter of the quadrupole coupling gives an unambiguous evaluation of double bond character in asymmetric molecules. This method is developed in a valuable paper by Bersohn.[19] The results of these workers show that the CCl bond has about 5 % double bond character when conjugated with a double bonded CC system. Thus it appears from table 4 that the π character is much greater when the conjugation is with a triple rather than with a double bond.

One relation, earlier evolved,[20] measures electronegativity in terms of the effective nuclear charge and the covalent radius, $z_{eff} . e/r$. The screening constant per valence electron which makes this scale agree with Pauling's was found to be 0.5. For a positive charge of c electron units on the atoms, the relation can be expressed as

$$x = 0.31 \frac{(n + 1 + c)}{r} + 0.50, \qquad (31)$$

where n is the number of electrons in the valence shell of the neutral atom and r is the covalent radius.

Let us now consider the spherical XY_4 molecules in which X is C, Si, Ge or Sn, and Y is Cl, Br or I. Quadrupole coupling data for all these combinations are now available. Although the data are for solid state, the fact that couplings in molecules such as CF_3Cl are almost identical in the solid and gaseous states

suggests that we can safely neglect effects of solid state interactions in these completely spherical molecules. If we let γ_π represent the amount of π character we can write $c = 4(\beta_\sigma - \gamma_\pi)$ and transform eqn. (31) to

$$x_{\mathbf{X}} = 0.31 \left[\frac{5 + 4(\beta_\sigma - \gamma_\pi)}{r} \right] + 0.50, \tag{32}$$

in which $n = 4$ has been substituted for the C, Si, Ge and Sn. Since γ_π will not be large here, we can regard x_{Hal} as constant and can neglect effects of any changes in Hal screening on ρ_q. We cannot likewise neglect changes in $x_{\mathbf{X}}$. Electrons are being sucked away from X in four directions, and its electronegativity will change according to eqn. (32). With the known values of x_{Hal}, r, and ρ_q, eqn. (29) and (32) were solved for γ_π, β_σ and $x_{\mathbf{X}}$. The results are shown in table 5.

TABLE 5.—BOND PROPERTIES PREDICTED FROM QUADRUPOLE COUPLINGS
AND ELECTRONEGATIVITIES

	coupling ratio obs. ρ_q	effective electro-negativity of central atom	π character (%)	ionic character of σ bond (%)	resultant ionic character $(\beta_\sigma \ \gamma_\pi)$ (%)	charge on central atom in electron units
B(CH₃)	0·10[a]	2·06	0	12	12	+ 0·36
BCl₃	0·39[b]	2·08	29	46	17	+ 0·51
CCl₄	0·75[b]	2·58	9	21	12	+ 0·48
CBr₄	0·83[c]	2·55	8	13	5	+ 0·20
CI₄	0·93[d]	2·50	4	5	1	+ 0·04
SiCl₄	0·37[b]	2·04	30	48	18	+ 0·72
SiBr₄	0·46[c]	1·98	26	41	15	+ 0·60
SiI₄	0·58[d]	1·96	20	32	12	+ 0·48
GeCl₄	0·47[b]	2·08	14	46	32	+ 1·28
GeBr₄	0·54[e]	2·03	12	39	27	+ 1·08
GeI₄	0·65[d]	2·00	9	30	21	+ 0·84
SnCl₄	0·44[b]	1·97	9	51	42	+ 1·68
SnBr₄	0·50[e]	1·91	8	45	37	+ 1·48
SnI₄	0·61[d]	1·87	6	37	31	+ 1·24

a Molecular coupling by Dehmelt (see tabulation in ref. (5)) with atomic coupling by Wessel, Physic. Rev., 1953, 92, 1581.
b Livingston (see tabulation in ref. (5)).
c Schawlow, J. Chem. Physics, 1954, 22, 1211.
d Robinson, Dehmelt and Gordy, J. Chem. Physics, 1954, 22, 511.
e Kojima, Tsukada, Ogawa and Shimanchi, J. Chem. Physics, 1953, 21, 1415.

The values in table 5 appear entirely consistent and reasonable. The π character of the individual bonds is shown diagrammatically in fig. 6. The trends agree in every respect with the qualitative predictions of Pauling [21] based upon considerations of interatomic distances alone—distances which were often very inaccurate. We might say that these results tend to substantiate the remarkable intuition of Pauling.

Perhaps some will be reluctant to accept relation (22) on the basis that it seems to require too much formal charge on certain atoms in polyatomic molecules. That molecules have a way of avoiding excessive charges without violating this relation can be seen from an examination of table 5. The methods seemingly employed by these molecules are electronegativity variation and negative feed back (π character). Note that the resultant ionic character $(\beta_\sigma - \gamma_\pi)$ given in column 6 is down to that to which people are accustomed.

One would suppose that the bonding in $A(Hal)_3$ molecules is similar to that of $X(Hal)_4$ molecules, but I cannot treat these molecules in the same way from solid state couplings because of their strong intermolecular dipole interactions which probably alter the couplings 10 to 15 %. I have ventured treatments similar to the above for the non-polar molecules BCl_3 and $B(CH_3)_3$ from solid state coupling. The results are given in table 5. That of $B(CH_3)_3$ is based on the B^{11} coupling for which distortion effects, not taken into account, may be significant. Note that π feed back is not detected for $B(CH_3)_3$ but is strong in BCl_3.
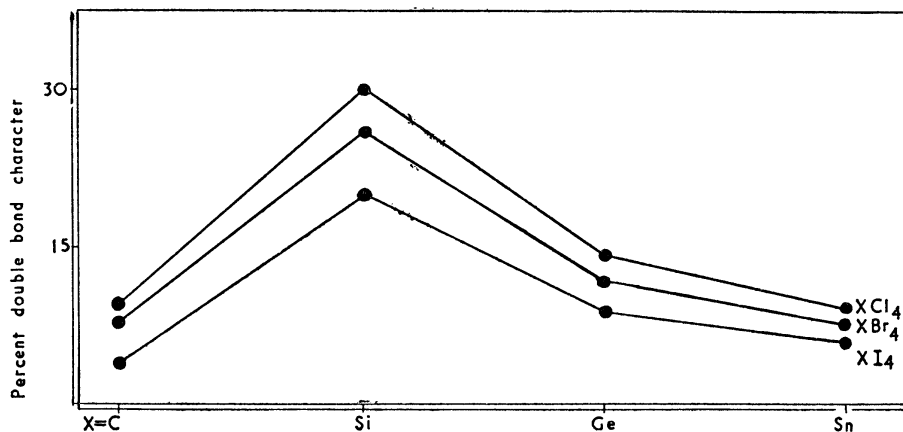

FIG. 6.—Plot of π character (double bond character) in C—Hal bonds.

Borine carbonyl, BH_3CO, is a strange sort of molecule. From its early micro-wave structural determination in our laboratory [22] it was concluded that the BC link in it is only about half a bond. Now that the atomic coupling per p electron has been measured, [23] we can conclude with fair assurance that the BC bond order is 0·6. This prediction still depends partly on the structure in that the bond orbital hybridization employed in the estimate is calculated from the HBH bond angle of 113° 58'.

Although I have found no quadrupole coupling nor dipole moment requirements for hybridization in bond orbitals of the halogens except possibly on the Cl and Br in FCl and FBr, where there is a positive (not a negative) charge on the halogen, the quadrupole couplings do not exclude the possibility of small amounts, the order 2 or 3 % s or d character, nor even larger amounts if there is approximately equal s and d hybridization. The evidence is against d hybridization on the negative ion, however. The quadrupole coupling of S^{33} in H_2S shows that unquestionably there is significant hybridization [24] of the S bonding orbitals despite the approximate right-angle of its bonds. The same applies to AsH_3 and SbH_3. To reconcile the bond angles in these molecules with the hybridization required by the coupling, it appears necessary to assume both s and d contribution or to treat the bonding in terms of delocalized molecular orbitals. These cases are treated elsewhere. [25]

The programme committee asked that we stress our personal interpretations. I have given here some of my own notions on what nuclear quadrupole couplings show us about the chemical bond. I think it appropriate to tell you that mine is not the only treatment. Townes and Dailey, who took the first look at quadrupole couplings of the halogens, [26] interpreted them as indicating 18 to 20 % s hybridization of the Cl bonding orbital. They later revised the estimates to include Br and I, but only when there is ionic character which gives the negative charge to the coupling Cl, Br or I. This latest interpretation is condensed in a rule given by Townes. [27] While confessing that the rule is a bit arbitrary, he states that quadrupole couplings appear to indicate the following type of variation :
" The halogen bonds are hybridized with 15 % s character whenever the halogen

is more electronegative by 0·3 unit than the atom to which it is bonded. Otherwise there is no hybridization."* As you can see, Townes and Dailey and I are at opposite poles on hybridization. As a result, our ionic characters are different.

In wrangling with these problems I have tried to keep in mind the power of the simple intuitive approach of Faraday, but I have been unable to forget a remark by Mulliken that molecules just aren't simple.

I regret that limitations of space prevent my giving proper reference to all the material I have used. It is a pleasure to acknowledge many helpful discussions of quadrupole couplings with Dr. H. Dehmelt. I wish to thank the U.S. National Science Foundation for a travel grant to attend this Discussion.

* In a paper published after this was written, Townes and Dailey keep the rule but change the dividing line to 0·25 unit (*J. Chem. Physics*, 1955, **23**, 118).

[1] Burrus and Gordy, *Physic. Rev.*, 1954, **93**, 897.

[2] Genzel and Eckhardt, *Z. Physik*, 1954, **139**, 592.

[3] Bitter, *Physic. Rev.*, 1949, **76**, 833.

[4] Kastler and Brossel, *Compt. rend.*, 1949, **229**, 1213.

[5] Gordy, Smith and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, New York, 1953).

[6] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493.

[7] This has been emphasized earlier by the author, and the inadequacy of the H.-L. and l.a.c.o. functions for calculating nuclear coupling has been pointed out (*J. Chem. Physics*, 1954, **22**, 1470).

[8] In effect, we here regard the atomic orbitals as divided into inner and outer parts. The inner parts, which account essentially for the nuclear coupling, have no overlap ($S_{ab} = 0$ for these parts) and suffer no reduction in the normalization of the total molecular orbital function, whereas the outer parts have overlap ($S_{ab} = 0$) and suffer distortions.

[9] Robinson, Dehmelt and Gordy, *J. Chem. Physics*, 1954, **22**, 511.

[10] Gordy, *J. Chem. Physics*, 1951, **19**, 792.

[11] Burrus and Gordy, *Physic. Rev.*, 1954, **92**, 1437; *Physic. Rev.*, 1954, **93**, 419. Burrus, Gordy, Benjamin and Livingston, *Physic. Rev.*, 1955 (in press).

[12] Pauling, *Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N.Y., 1939), chap. 2.

[13] Mulliken, *J. Chim. Phys.*, 1949, **46**, 497.

[14] Coulson, *Valence* (Clarendon Press, Oxford, 1952), p. 206.

[15] Debye, *Polar Molecules* (reprint by Dover Publications, New York, 1945), p. 60.

[16] Gordy, *J. Chem. Physics*, 1946, **14**, 305.

[17] Herzberg, *Infra-red and Raman Spectra* (D. van Nostrand Co., New York, 1945), p. 180.

[18] Goldstein and Bragg, *Physic. Rev.*, 1950, **78**, 347.

[19] Bersohn, *J. Chem. Physics*, 1954, **22**, 2078.

[20] Gordy, *Physic. Rev.*, 1946, **69**, 604.

[21] Pauling, ref. (12), chap. 7.

[22] Gordy, Ring and Burg, *Physic. Rev.*, 1950, **78**, 512.

[23] Wessel, *Physic. Rev.*, 1953, **92**, 1581.

[24] Burrus and Gordy, *Physic. Rev.*, 1953, **92**, 274.

[25] Weissberger and West (ed.), *Chemical Applications of Spectroscopy* (Interscience Publishers, New York, in press), chap. 2 (W. Gordy).

[26] Townes and Dailey, *J. Chem. Physics*, 1949, **17**, 782.

[27] Townes in *Symposium on Molecular Physics* (Maruzen Co., Ltd., Tokyo, 1954), p. 105. This rule is adhered to in a more recent publication (Townes and Dailey, *J. Chem. Physics*, 1955, **23**, 118).