# Infrared Intensities. The Methyl Halides. Effect of Substituents on Charge Distributions

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**Abstract:** The geometries, force constants, and dipole moment derivatives for methyl fluoride and chloride were calculated using several basis sets. The 4-31G set gave unsatisfactory geometries and dipole moments. The addition of either bond functions or polarization functions led to essentially the same geometrical parameters and dipole moments for both methyl halides which were in agreement with experimental data. Both extended basis sets gave the same dipole moment derivatives which agreed with the experimentally derived values. It is shown that there is a significant difference between the nature of a C–F and a C–Cl bond. Fluorine withdraws charge from the carbon, but does not significantly affect the charge on the hydrogen of the methyl fluoride. Chlorine withdraws charges from both the carbon and the hydrogen in methyl chloride. The dipole moment derivatives are discussed in terms of a rehybridization model.

The question of the effect of substituents on the charge distribution in molecules remains unanswered. Some theoretical calculations suggest that charge alternation should appear in a saturated hydrocarbon chain, analogous to that found in conjugated $\pi$-electron systems.[1] Experimental studies suggest that the substituents operate almost exclusively via the field effect which depends only on geometry.[2] $^{13}$C NMR chemical shifts are almost always upfield at the $\gamma$ position to an electron-withdrawing substituent suggesting that the electron density may have been increased by the substituent.[3] Through-bond effects of the type discussed by Hoffmann[4] may also be important, and would provide another mechanism for charge redistribution.

It now seems possible to approach this important problem by a combination of experimental and theoretical methods. The intensities of infrared bands may be used to derive dipole moment/coordinate derivatives which in turn may be related to the individual bond dipoles in a molecule.[5] Theoretical calculations will yield charge distributions, but there always remains the question of the adequacy of the basis set which was used. This can be answered by calculating the dipole moment derivatives. Agreement with the experimental values will indicate that the calculated charge distribution is essentially correct.

We have initiated a study of this problem, and we now present the results obtained with the simplest system, the methyl halides. Here, experimental data are already available for comparison with the theoretical calculations.[6,7] A study of these compounds should indicate how the $\alpha$ hydrogens are affected by halogen substituents.

The results obtained for methyl fluoride are given in Table I. The symmetry coordinates are summarized in Table II. The molecule was oriented with the fluorine along the $+z$ direction so that the sign of the dipole moment would be negative. It can be seen that the 4-31G basis set,[8] which is usually satisfactory for hydrocarbons,[9] gives an unsatisfactory geometry and dipole moment.[10] This is not surprising since the basis set constrains the atomic orbitals to be symmetrical with respect to the corresponding nuclei. When two atoms having markedly different electronegativity are joined, the atomic orbitals will be polarized by the resultant field. The basis set may be appropriately extended either by the use of bond functions (BF)[11] located at the midpoints of the C–H and C–F bonds,[12] or by the use of d orbitals as polarization functions (6-31G*).[13] Both sets lead to markedly improved geometries and dipole moments, which are in satisfactory agreement with the observed values. It must be remembered that the calculated bond lengths represent the bottom of the potential well whereas the observed lengths are longer because of anharmonicity. In the case of methane the observed C–H bond length is 1.093 Å[14] whereas when corrected for anharmonicity it is 1.088 Å.[15]

The force constants obtained using the 6-31G* basis set are uniformly about 10% too large, as is commonly observed.[16] The dipole moment derivatives obtained using the two extended basis sets are essentially the same despite the significantly lower calculated total energy using the 6-31G* set. The agreement between the values suggests that larger basis sets are unlikely to lead to significant changes in the calculated values.

The observed intensities of the infrared bands are related to $|\partial\mu/\partial Q_i|^2$ where $Q_i$ is the normal coordinate for the motion which leads to the band. The quantities of interest are $\partial\mu/\partial S_j$ where $S_j$ is a symmetry coordinate (Table II). They are obtained from $\partial\mu/\partial Q_i$ by

$$\frac{\partial\mu}{\partial S_j} = \sum_i L_{ij}{}^{-1}\frac{\partial\mu}{\partial Q_i}$$

The $L_{ij}{}^{-1}$ terms are the elements of the $L^{-1}$ matrix which is obtained as part of a normal coordinate analysis. A major problem in obtaining the $\partial\mu/\partial S_j$ is the lack of information concerning the signs of $\partial\mu/\partial Q_i$. The sign of $\partial\mu/\partial S_1$ must be positive since the C–H bond is polarized C$^-$–H$^+$ and on stretching must approach electrical neutrality.[5] The calculations in all cases lead to a negative sign for $\partial\mu/\partial S_3$. If these signs are accepted, only one sign combination for the $\partial\mu/\partial Q_i$ (+−−, $i$ = 1–3) will give consistent values for $CH_3F$ and $CD_3F$. The combination has been commonly accepted.[7,17] The calculated values of $\partial\mu/\partial S_1$ through $\partial\mu/\partial S_3$ are in very good agreement with the values obtained experimentally suggesting that the corresponding wave functions correctly represent the electron density distribution.

The degenerate modes ($S_4$–$S_6$) present more of a problem. It is clear that $\partial\mu/\partial S_4$ should have a positive sign in correspondence with $\partial\mu/\partial S_1$. With this sign choice and the requirement of agreement between values derived from $CH_3F$ and $CD_3F$, there are two possible sign choices for the $\partial\mu/\partial Q_i$, (+−−) and (+−+) (Table III). A study of interaction between vibrational modes led di Lauro and Mills[18] to conclude that $\partial\mu/\partial Q_2$ and $\partial\mu/\partial Q_5$ should have the same sign. A similar conclusion was reached for $\partial\mu/\partial Q_3$ and $\partial\mu/\partial Q_6$. Since the sign combination (−−−) gives the wrong sign for $\partial\mu/\partial S_4$, this is strong evidence for the (+−−) set, and it gives better agreement with the calculated values than does the (+−+) set. There is, unfortunately, a large uncertainty associated with the $\partial\mu/\partial S$ for methyl fluoride which arises from the strong overlap of the vibrational bands and the difficulty of separating the intensities associated with each of them.[7] A further refinement of the experimental data would be very helpful.

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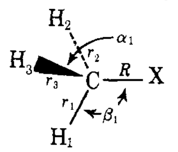
**Table I.** Results of Methyl Fluoride Calculations

| parameter | 4-31G | basis set<br>4-31 G + BF | 6-31G* | obsd |
|---|---|---|---|---|
| $r_{C-X}$, Å | 1.412 | 1.373 | 1.365 | 1.382[a] |
| $r_{C-H}$, Å | 1.077 | 1.088 | 1.083 | 1.095 |
| ∢H-C-F, deg | 108.27 | 108.99 | 109.05 | 108.42 |
| $\mu$, D | 2.64 | 1.96 | 1.99 | 1.86[b] |
| $E$, au | −138.858 61 | −138.895 49 | −139.034 61 | |
| $k_1$, mdyn/Å | 6.23 | 6.11 | 5.89 | 5.25[c] |
| $k_2$ | 0.82 | 0.82 | 0.84 | 0.76 |
| $k_3$ | 6.05 | 7.06 | 6.62 | 5.69 |
| $k_4$ | 5.70 | 5.58 | 5.65 | 5.28 |
| $k_5$ | 0.70 | 0.68 | 0.69 | 0.58 |
| $k_6$ | 1.07 | 1.01 | 1.04 | 0.91 |
| $\partial\mu/\partial S_1$, D/Å | 0.48 | 0.68 | 0.67 | 0.52 ± 0.14[d] |
| $\partial\mu/\partial S_2$ | −0.01 | −0.05 | −0.05 | 0.09 ± 0.10 |
| $\partial\mu/\partial S_3$ | −4.13 | −4.97 | −4.90 | −4.50 ± 0.58 |
| $\partial\mu/\partial S_4$ | 0.84 | 1.20 | 1.06 | 0.77 ± 0.08 |
| $\partial\mu/\partial S_5$ | −0.30 | −0.12 | −0.14 | −0.30 ± 0.08 |
| $\partial\mu/\partial S_6$ | 0.06 | −0.13 | −0.10<br>(−0.08)[e] | 0.12 ± 0.24 |

[a] Reference 14. [b] Nelson, R. D., Jr.; Lide, D. R., Jr.; Margott, A. A. "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", National Bureau of Standards: Washington, D.C., 1967. [c] Reference 6. [d] Twice the uncertainties based on the experimental data to correspond roughly to the 90% confidence level. [e] 6-31G** result.

**Table II.** Symmetry Coordinates for Methyl Halides



$$S_1 = (1/\sqrt{3})\,(\Delta r_1 + \Delta r_2 + \Delta r_3)$$
$$S_2 = [-2/\sqrt{6}\,(P + Q)]\,(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)^{a}$$
$$S_3 = \Delta R$$
$$S_4 = (1/\sqrt{6})(2\Delta r_1 - \Delta r_2 - \Delta r_3)$$
$$S_5 = (1/\sqrt{6})(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$$
$$S_6 = (1/\sqrt{6})(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$

[a] $P$ and $Q$ are normalization factors defined in ref 7.

**Table III.** Experimental Dipole Moment Derivatives for the Degenerate Modes of Methyl Fluoride and Chloride[a]

| X | signs | $S$ | $\partial\mu/\partial S$<br>$CH_3X$ | <br>$CD_3X$ | <br>av |
|---|---|---|---|---|---|
| F | +−− | 4 | 0.73 ± 0.08[b] | 0.80 ± 0.04[b] | 0.77 ± 0.08[c] |
| | | 5 | −0.27 ± 0.02 | −0.34 ± 0.09 | −0.30 ± 0.08 |
| | | 6 | 0.00 ± 0.03 | 0.24 ± 0.03 | 0.12 ± 0.24 |
| F | +−+ | 4 | 0.77 ± 0.03 | 0.84 ± 0.04 | 0.80 ± 0.08 |
| | | 5 | −0.34 ± 0.02 | −0.34 ± 0.09 | −0.34 ± 0.04 |
| | | 6 | 0.36 ± 0.03 | 0.42 ± 0.03 | 0.39 ± 0.06 |
| Cl | +−− | 4 | 0.24 ± 0.01 | 0.24 ± 0.01 | 0.24 ± 0.01 |
| | | 5 | −0.26 ± 0.01 | −0.34 ± 0.01 | −0.30 ± 0.08 |
| | | 6 | −0.16 ± 0.01 | −0.01 ± 0.04 | −0.08 ± 0.16 |
| Cl | +−+ | 4 | 0.30 ± 0.01 | 0.30 ± 0.01 | 0.30 ± 0.01 |
| | | 5 | −0.36 ± 0.01 | −0.38 ± 0.01 | −0.37 ± 0.02 |
| | | 6 | 0.30 ± 0.01 | 0.33 ± 0.04 | 0.31 ± 0.03 |

[a] The rotational corrections were taken from Russel, Needham, and Overend, ref 7. [b] Uncertainties based on estimated errors in experimental data. [c] Twice the uncertainties based on the experimental data to correspond roughly to the 90% confidence level.

The antisymmetric H-C-X bending mode, $S_6$, is unique since it cannot be represented by a simple rehybridization scheme. Since the H-C-H angles remain constant, the CH bond orbitals cannot rehybridize. However, this is inconsistent with the changes in the H-C-F angles which require CH rehybridization. It was possible that this case might not be adequately represented by even the 6-31G* basis set, and so the calculation was repeated with p orbitals added to the hydrogens (6-31G**). This did not lead to a significant change in either the dipole moment or the dipole moment derivative. It appears unlikely that a further extension of the basis set will significantly change the calculated value of $\partial\mu/\partial S_6$.

The results for methyl chloride are given in Table IV. Again, the 4-31G basis set gives an unsatisfactory geometry and dipole moment.[10] The addition of bond functions to the basis set leads to markedly improved values. The force constants are in good agreement with the observed values, especially if they are scaled down by 10%. The calculated dipole moment derivatives change considerably on going from the 4-31G to the 4-31G + BF basis set, and there is not as good agreement with the observed values as found with methyl fluoride.

In order to gain more information concerning the system, other basis sets were examined. The STO-4G* set in which the STO-4G basis has been augmented by d orbitals at chlorine gave a very satisfactory geometry and dipole moment. However, the force constants were much less satisfactory, and the dipole moment derivatives were considerably different from those obtained using the other basis sets. The results are not surprising since this basis does not give much flexibility to the orbitals on carbon and hydrogen.

A split-valence basis set augmented by d orbitals at both carbon and chlorine would be desirable. The equivalent of a 6-31G* basis for chlorine has not been defined. We have used the 6-31G* basis for carbon and hydrogen, and Dunning's partially contracted basis for chlorine[19] augmented by a set of d orbitals.[20] The results also are shown in Table IV. The total energy is markedly lower than that for the other basis sets, largely because of the better description of the inner electrons. The geometry is similar to that for the 4-31G + BF basis, and the calculated force constants are in very good agreement. Again, they are about 10% larger than the observed values.

The calculated dipole moment derivatives for $S_1$-$S_3$ are in good agreement for the more extended basis sets, and the values are in satisfactory agreement with the experimental values. The (+−−) sign combination for the $\partial\mu/\partial Q$ was used for the same reasons as given for methyl fluoride. The calculated $\partial\mu/\partial S$ for $S_4$-$S_6$ also are in good agreement with the observed values if the (+−+) sign combination is taken. This is in accord with the observation of di Lauro and Mills[18] that $\partial\mu/\partial Q_2$ and $\partial\mu/\partial Q_5$ should have the same sign. It does not agree with the sign combination for methyl fluoride which best fits the calculated values, but there is no necessity for such agreement.

In order to interpret these results, an estimate of the C-H bond dipoles is needed. It is difficult to obtain charge distributions from molecular wave functions. The commonly employed Mulliken population analysis[21] partitions the electron density in an arbitrary fashion which is dependent on the basis set used. However, as long as the same basis set is used and the geometry remains essentially constant, the charge shifts at the hydrogens caused by substituents should be meaningful. The data are summarized in Table V.

We have previously presented evidence suggesting that the C-H bond dipole in methane is 0.55 D.[5] Using the point dipole

**Table IV.** Results of Methyl Chloride Calculations

| parameter | 4-31G | basis set<br>STO-4G* | 4-31G + BF | 6-31G* | obsd |
|---|---|---|---|---|---|
| $r_{C-X}$, Å | 1.877 | 1.773 | 1.792 | 1.806 | 1.778[a] |
| $r_{C-H}$, Å | 1.073 | 1.087 | 1.085 | 1.076 | 1.084 |
| ∢H-C-Cl, deg | 106.78 | 109.14 | 108.54 | 107.97 | 108.42 |
| $\mu$, D | 2.73 | 1.80 | 2.09 | 2.33 | 1.94[b] |
| $E$, au | −498.542 78 | −498.589 10 | −498.575 10 | −499.114 71 | |
| $k_1$, mdyn/Å | 6.18 | 7.26 | 5.80 | 5.96 | 5.49[c] |
| $k_2$ | 0.70 | 0.84 | 0.71 | 0.72 | 0.64 |
| $k_3$ | 3.00 | 5.36 | 3.97 | 3.79 | 3.50 |
| $k_4$ | 5.91 | | 5.85 | 5.88 | 5.36 |
| $k_5$ | 0.68 | | 0.66 | 0.67 | 0.54 |
| $k_6$ | 0.78 | | 0.83 | 0.81 | 0.72 |
| $\partial\mu/\partial S_1$, D/Å | 0.48 | −0.23 | 0.78 | 0.78 | 0.60 ± 0.04[d] |
| $\partial\mu/\partial S_2$ | −0.30 | −0.21 | −0.39 | −0.40 | −0.17 ± 0.04 |
| $\partial\mu/\partial S_3$ | −3.04 | −2.46 | −3.17 | −2.97 | −2.15 ± 0.14 |
| $\partial\mu/\partial S_4$ | 0.34 | | 0.69 | 0.43 | 0.30 ± 0.01 |
| $\partial\mu/\partial S_5$ | −0.47 | | −0.28 | −0.34 | −0.37 ± 0.02 |
| $\partial\mu/\partial S_6$ | 0.40 | | 0.28 | 0.38 | 0.31 ± 0.03 |

[a] Reference 14. [b] Footnote *b*, Table I. [c] Reference 6. [d] Twice the uncertainties based on the experimental data to correspond roughly to the 90% confidence level.

**Table V.** Calculated Charges for Methyl Halides

| basis set | compd | $q$(X) | $q$(C) | $q$(H) | $\mu_{CH}$ | eff $q$(CH) |
|---|---|---|---|---|---|---|
| 4-31G | methane | | −0.608 | +0.152 | 0.55[a] | +0.11[b] |
| | methyl fluoride | −0.464 | −0.035 | +0.166 | 0.55[c] | +0.11 |
| | methyl chloride | −0.157 | −0.501 | +0.220 | 0.75[c] | +0.15 |
| 6-31G* | methane | | −0.660 | +0.165 | | |
| | methyl fluoride | −0.400 | −0.064 | +0.155 | | |
| | methyl chloride | −0.278 | −0.439 | +0.239 | | |
| 4-31G + BF[d] | methane | | −0.356 | +0.102 | | |
| | methyl fluoride | −0.335 | +0.059 | +0.092 | | |
| | methyl chloride | −0.048 | −0.361 | +0.137 | | |

[a] Cf. ref 5. [b] Based on point-dipole approximation. [c] Estimated values based on the methane and methyl halide hydrogen charges. [d] The bond function electron densities were divided equally between the two atoms forming the bond.

approximation, this corresponds to a charge on the hydrogen of +0.11 electrons. The 4-31G and 6-31G* basis sets give essentially the same values for methane, +0.16 electron. The deficiency in electron density found in the calculation arises from the relatively large size of the "1" orbital at carbon in the 31 part of the basis set. Electron density residing in this orbital is assigned to carbon despite its penetration into the space which might reasonably be assigned to the proton. If the electron density associated with the bond function in the 4-31G + BF basis set is equally partitioned between the carbon and hydrogen, the calculated charge at hydrogen (+0.10) is too small. Since the carbon is considerably larger than the proton, it would be reasonable to assign more than half of the bond function electron density to the carbon. The experimental charge on hydrogen is between the two values obtained using a population analysis, indicating that the calculated charges for methane have reasonable magnitudes.

The introduction of a fluorine has a remarkably small effect on the hydrogen charge. The negative charge at fluorine appears to arise essentially completely from the carbon. A chlorine substituent, on the other hand, does withdraw electron density from the hydrogens. This probably corresponds to a normal effect of an electron-withdrawing substituent, and the small effect noted with fluorine is probably due to back-bonding by the fluorine via its lone pairs.[22] Such an interaction is much less likely with chlorine because of the difference in principal quantum number between carbon and chlorine. These calculations suggest that the charge on the protons of methyl fluoride is essentially the same as in methane[5] and $\mu_{CH}$ is therefore estimated as 0.55 D. In the case of methyl chloride, the charge on the protons appears to be about 0.04 e greater, leading to an estimated $\mu_{CH}$ of 0.75 D.

Let us first consider the bond stretching modes, $S_1$, $S_3$, and $S_4$. With the symmetric C-H stretching mode, $S_1$, the sign of the calculated $\partial\mu/\partial S_1$ indicates that the electron density at hydrogen increases with bond stretching, and results from preferred homolytic dissociation. The charge shift derived from the population analysis is in accord with this conclusion. A similar pattern is found with the antisymmetric stretching mode, $S_4$. Here, the C-H bond which is extended leads to an increase in hydrogen electron density whereas those which are compressed lead to a corresponding decrease in electron density.

The case of the C-X stretching mode, $S_3$, is quite different. The sign of $\partial\mu/\partial S_3$ as well as the calculated charge shifts for the halogens indicates that the charge on the halogen becomes more negative as the C-X bond is extended. All of the methyl halides prefer to dissociate homolytically (for methyl chloride the homolytic bond dissociation energy is 84 kcal/mol whereas the heterolytic dissociation energy ($CH_3^+$ $Cl^-$) is 223 kcal/mol[23]). Despite this preference, at distances near the equilibrium length electron density increases at halogen with increasing C-X distance.

The bending modes, $S_2$, $S_5$, and $S_6$, are more closely related to the bond dipoles than are the stretching modes.[5] The simplest model for these modes assumes that the CH bond dipoles have fixed values. Geometrical considerations then lead to the following expressions:[17]

$$\partial\mu/\partial S_2 = \sqrt{1.5}\sin\beta\cdot\mu_{\mathrm{CH}}$$

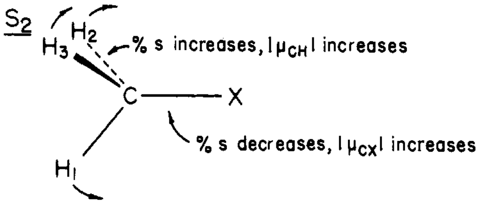
$$\partial\mu/\partial S_5 = -\sqrt{2}\cos(\alpha/2)\cdot\mu_{\mathrm{CH}}$$

$$\partial\mu/\partial S_6 = -\sqrt{6}\cos\beta\cdot\mu_{\mathrm{CH}}$$

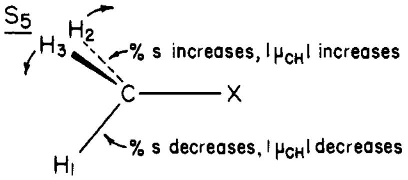
Using the estimated values of $\mu_{\mathrm{CH}}$ from Table V, this model gives the values 0.64, −0.44, and 0.43 for the three modes of methyl fluoride and 0.87, −0.60, and 0.58 for methyl chloride. It can be seen that this simple calculation does not give results in good agreement with the experimental values (Tables I and IV). The latter have a smaller magnitude than expected based on this model.

Our analysis of the bending modes of ethylene indicated the importance of rehybridization in determining $\partial\mu/\partial S$.[5] The calculated charge shifts for these modes of the methyl halides were found to be considerably smaller than for the stretching modes, and were inconsistent between basis sets. This results from the arbitrary way in which charge is assigned in a population analysis. Since the charge shifts could not be used as a guide to changes in hybridization, we shall present a qualitative description of the expected changes.

Let us first consider the symmetric bending mode, $S_2$. A positive change in the symmetry coordinate will lead to an increase in the H-C-H angle and a corresponding increase in the % s character of the C-H bonds. This will lead to an increase in $|\mu_{\mathrm{CH}}|$ which will result in a decrease in $\partial\mu/\partial S_2$ (i.e., the increase in $|\mu_{\mathrm{CH}}|$ will lead to a smaller change in the $\mu_{\mathrm{CH}}$ component along the $z$ axis than would be expected from the change in geometry). At the same time, the H-C-X angle decreases leading to a decrease in the % s character of the C-X bond. This will lead to an increase in $|\mu_{\mathrm{CX}}|$, and again will decrease $\partial\mu/\partial S_2$. The net effect of these two rehybridization components is to reduce $\partial\mu/\partial S_2$ to a value close to zero for methyl fluoride, and to a negative value for methyl chloride.



The antisymmetric H-C-H bending mode, $S_5$, may be considered in the same fashion. An increase in the $H_2$-C-$H_3$ angle will result in an increase in s character and an increase in $\mu_{\mathrm{CH}}$, whereas the decrease in the H-C-H angles involving $H_1$ will have the opposite effect on the C-$H_1$ bond. The increase in $\mu_{\mathrm{CH}}$ for C-$H_2$ and C-$H_3$ as well as the decrease in $\mu_{\mathrm{CH}}$ for C-$H_1$ will combine to lead to a reduced $\partial\mu/\partial S_5$. The decrease is considerably less than that observed for $S_2$. The experimental $\partial\mu/\partial S_5$ then gives a lower limit to $\mu_{\mathrm{CH}}$ and suggests that the values estimated in Table V are reasonable.



The antisymmetric H-C-X bending mode, $S_6$, is not easily described in terms of a rehybridization argument. As indicated above, the constancy of the H-C-H angles suggests no rehybridization in the CH bonds, whereas the changes in the H-C-X angles require some rehybridization. We will not further consider this mode at the present time.

The data presented above indicate that wave functions which satisfactorily reproduce the electron density distribution may be obtained for methyl fluoride and methyl chloride using an extended basis set. The 4-31G + BF basis appears to be a cost-effective alternative to a 6-31G* basis. The interaction between the halogen and the carbon-hydrogen bonds appears to be quite different for the two halides. Rehybridization arguments have some success in interpreting the dipole moment derivatives.

We are now extending this study to the ethyl, 1-propyl, and 1-butyl halides so that the effect of halogen substituents on charges may be determined for different positions and as a function of conformation. The effect of overlap of the halogen orbitals with the β, γ and δ C-H bonds should be minimal and an examination of charge shifts based on a population analysis should be simplified. At the same time, we are examining ways of obtaining charge shifts directly from the electron density distributions derived from the wave functions.

**Calculations.** The calculations were carried out using GAUSSIAN-70[24] and GAUSSIAN-76[25] and the standard 4-31G, 6-31G*, and 6-31G** basis sets. In the case of chlorine, the basis set of Dunning's, augmented by d functions,[19,20] was used along with the 6-31G* basis for carbon and hydrogen. The force constants and dipole moment derivatives were evaluated numerically using 0.02 Å or 2° distortions about the equilibrium geometry.

**Acknowledgment.** This investigation was supported by the Office of Basic Energy Sciences, Department of Energy. We thank Professor J. A. Pople for making GAUSSIAN-76 available before its general release.

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# Unified Theory of Resonance Energies, Ring Currents, and Aromatic Character in the $(4n + 2)\pi$-Electron Annulenes

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*Received October 23, 1978*

**Abstract:** It is demonstrated for the first time that, to high accuracy, there is an analytic relationship between the resonance energies (REs) and reduced ring currents (RCs) of the $(4n + 2)\pi$-electron annulenes—the original subjects of the Hückel rule—which leads naturally to a unified theory of aromatic character. The resonance energy is obtained as RE = $\pi^2 p_{rs}\beta/3N = \pi^2 E/6N^2$ where $p_{rs}$ is the bond order, $N$ is the number of carbon atoms, $E$ is the total $\pi$-electron energy, and $\beta$ is the resonance integral. The relationship between resonance energies and ring currents takes the form RE = $\pi^2$RC$/3S$ or RC = $3S$ RE$/\pi^2$ where $S$ is the area of the ring. The available experimental evidence is shown to be in excellent agreement with this relationship. Attention is drawn to the present lack of integrity of our knowledge of nondissipative currents in organic molecules and bulk superconductors, and common facets of present theories are discussed.

While aromatic character has been of interest for some time,[1-6] attempts to quantify and more closely define the subject have considerably intensified in recent years. This is particularly true in the area of resonance energies, which are often interpreted in terms of aromatic character. The impetus for this revival of interest came from the work of Dewar,[7-12] in which he redefined the reference energy for calculation of the energy of aromatic stabilization. His method employs the appropriate number of localized single and double bond energies (taken from a series of polyenes) for the calculation of a reference energy which is defined to be the nonaromatic energy of the particular system.[7-12] With this definition the annulenes were found to possess a wide and continuous spectrum of resonance energies which included both positive (aromatic) and negative (antiaromatic[7,8]) values.[7-12] These quantities (which are now termed Dewar resonance energies) were first calculated by Dewar within the framework of the PMO theory and a $\pi$-electron SCF MO method.[8-12] More recently Hess and Schaad (HS)[13-17] have reparametrized the Hückel molecular orbital (HMO) method in a way which allows the calculation of Dewar resonance energies. A variation of this approach was introduced by Aihara (A-I and A-II)[18-20] and Gutman, Milun, and Trinajstic (GMT),[21] who utilized the $\pi$-bond energy of an infinitely large cyclic polyene in their definition of a reference structure. This procedure obviates the need for the utilization of a Kekule structure with distinct single and double bonds (which may not be unique), and ensures the correct asymptotic nonaromatic limit at infinitely large ring size. Finally, using a valence bond approach, Herndon[22-25] has introduced a structure-resonance theory based on Kekule structures which also allows the calculation of resonance energies.

The results of all of these methods are not only in good agreement with one another but have been demonstrated by the authors to provide a rather reliable index of the chemical stability and reactivity of the compounds studied.[9-25] Insofar as resonance energies serve as a criterion of aromatic character it may therefore be concluded that this aspect of the subject is now well understood. This in turn has led to a great improvement in our conception of the Hückel $(4n + 2)\pi$-electron rule.

The current state of affairs with other criteria of aromatic character is nowhere near as satisfactory. This is particularly true of the magnetic or ring current criterion of aromaticity.[2-4,6,26-40] Of all the criteria this one is most often employed, as some measure of the ring current is usually available from the $^1$H NMR (and sometimes $^{13}$C NMR[41-43]) chemical shifts[4] of the compound, and measurements of diamagnetic susceptibility exaltations[44] seem to be becoming quite routine.[45] In fact the magnetic criterion is often the sole piece of evidence for the aromatic character of new compounds, as resonance energies are extremely difficult to measure experimentally and are usually inferred from the observed chemical stability (which is not necessarily directly related to ground-state quantities such as resonance energy). There is now strong evidence to suggest that there is no relationship among these different criteria of aromatic character in the case of nonalternant hydrocarbons and heteroatomic systems.[26-30] *Even for the alternant hydrocarbons and annulenes there is as yet no demonstrated relationship between ring currents and resonance energies*, although the qualitative connection seems soundly based.[40] It is the purpose of this paper to show that there is in fact a direct mathematical dependence between these two quantities which allows the development of a unified theory of aromatic character in the $(4n + 2)\pi$-electron annulenes (which, after all, are the original subject of the Hückel rule).

Also included in the present work is a reconsideration of molecular ring currents[33,34] in the light of the microscopic theory of superconductivity as developed by Bardeen, Cooper, and Schrieffer (BCS).[46]

## Theory

**1. General.** The Hückel molecular orbitals[11,47-49] for $\pi$-