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Electronic States of Organic Molecules. 6. Analysis of Infrared Intensities. The Hybrid Orbital Rehybridization Model. Charge Distribution in Molecules¹

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Abstract: A general model for analysis of infrared intensities is proposed and applied to a series of organic molecules. This model, called the hybrid orbital rehybridization model (HORM), splits the infrared intensity into a static term due to geometric reorientation of the bond moments and a dynamic term arising from bond rehybridization. A linear dependence between CH bond moments and % s character is observed, and explicit formulas are proposed for the rehybridization components. Criteria for determining which vibrational modes are purely geometric are developed, then used in conjunction with ab initio calculations to obtain values of the CH and CC bond dipoles for series of compounds. Charge distributions in these molecules are also deduced from these results.

I. Introduction

The positions and intensities of infrared bands potentially contain a great deal of information about both static molecular structure and normal vibrations. However, while much progress has been made in extracting information from line positions,² the corresponding analysis of intensities is generally quite crude.³ In the case of line positions, the harmonic oscillator model provides a reasonable physical picture for qualitative and quantitative analysis. On the other hand, the results of previous analyses³ suggest that the most obvious parameters for infrared intensities—effective bond moments and atomic charges—do not provide an internally consistent basis for interpretation. Various other types of parametrization have, in fact, been able to reproduce experimental intensities, but they generally lack physical interpretation or are not easily generalized.³

In the present work, a general model for infrared intensities which overcomes these difficulties is proposed. This model separates the intensity into a static term due to effective bond moments, and a dynamic term arising from charge rearrangement. Both terms are shown to be functions of the hybridization, and explicit expressions for their evaluation are proposed. The key element in the derivation of this model is a combination of extended basis ab initio intensity calculations with the experimental intensities of small hydrocarbons. One of the more important results of this method is the development of a set of criteria which characterize vibrations whose intensity is due to purely geometric rearrangement of the bond moments.

These criteria, coupled with the fact that such vibrations will be the most intense, provide a powerful tool for the analysis of infrared spectra.

A proper presentation of this model requires a somewhat detailed review of the previous work on infrared intensities, and this is given in section II. In section III, the general hybrid orbital rehybridization model (HORM) is developed, while specific evaluation of parameters is considered in section IV. The use of ab initio localized molecular orbitals to obtain bond moments is treated in section V, while in section VI bond moments calculated with HORM are compared with additional experimental estimates.

II. Theory and Previous Work

The experimentally measured quantity corresponding to the infrared intensity is the absolute absorption coefficient. A_i . For a transition from the i th to the $i + 1$ vibrational state, it is given by

$$A_i = \frac{8\pi^2 N \nu_i}{3hc} \sum_i g_i |\langle i+1 | \mu | i \rangle|^2 \quad (1)$$

where N is Avogadro's number, ν_i is the transition frequency, h is Planck's constant, c is the velocity of light, and μ is the dipole moment operator. The sum on i is over the g_i degenerate states. Under the assumption of electrical and mechanical harmonicity, A_i becomes⁴

$$A_i = \frac{N\pi g_i}{3c^2} \left| \frac{\partial \mu}{\partial Q_i} \right|^2 \quad (2)$$

The set of normal coordinates, Q_i , describes the vibrational modes in a representation which diagonalizes the kinetic and potential energy matrices. Written in terms of a linear combination of internal coordinates $\{q_i\}$ (i.e., bond lengths and bond angles), the $\{Q_i\}$ are difficult to work with. To simplify the calculations, the $\{Q_i\}$ are expressed in terms of the symmetry coordinates $\{S_j\}$. Each S_j is an appropriate linear combination of $\{q_i\}$ which transforms as the irreducible representation of the molecule. They are related to the $\{Q_i\}$ by the matrix equation

$$\mathbf{Q} = \mathbf{L}\mathbf{S} \quad (3)$$

where \mathbf{L} is the matrix of the transformation coefficients defined in the usual Wilson FG formalism.⁵ In terms of symmetry coordinates, the $\{\partial\mu/\partial Q_i\}$ become

$$\frac{\partial\mu}{\partial Q_i} = \sum_j L_{ji} \frac{\partial\mu}{\partial S_j} \quad (4)$$

or conversely

$$\frac{\partial\mu}{\partial S_j} = \sum_i L_{ij}^{-1} \frac{\partial\mu}{\partial Q_i} \quad (5)$$

L_{ji} is the j,i th element of \mathbf{L} and $\mathbf{L}\mathbf{L}^{-1} = 1$.

A particularly useful subset of $\{S_j\}$ is the set of semisymmetry coordinates $\{S_i'\}$. Each $\{S_i'\}$ is composed of a linear combination of coordinates of the same type associated with a given chemical group (e.g., all $\text{C}=\text{C}_a\text{-H}$ angles on center a in ethylene). The $\{S_i'\}$ are chosen so as to form a basis for the $\{S_j\}$. Equations analogous to 4 and 5 can be written where S_j is replaced by S_i' and L by L' , etc.

The quantum mechanical evaluation of $\partial\mu/\partial Q_i$ proceeds by first calculating all $\partial\mu/\partial S_j$ and then using eq 4 to get $\partial\mu/\partial Q_i$. The $\partial\mu/\partial S_j$ are numerically approximated by

$$\frac{\partial\mu}{\partial S_j} = \frac{\mu(S_j) - \mu(S_j = 0)}{\Delta S_j} \quad (6)$$

where $\mu(S_j)$ is μ calculated for some deformation along S_j . For bending coordinates, each S_j is calculated for q_i taken at 2 and 4° while for stretches each q_i is 0.01 and 0.02 Å. Under the approximation of electrical harmonicity, μ should be linear in S_j , with slope $\partial\mu/\partial S_j$, since

$$\mu \approx \mu^0 + \frac{\partial\mu}{\partial S_j} \Delta S_j \quad (7)$$

Several different units are in use for infrared intensities.³ The present work writes all $\partial\mu/\partial S_j$ in $\text{D}/\text{Å}$, with all bends assumed scaled by $r_0 = 1.0 \text{ Å}$.

The analysis of infrared intensities is dependent on the availability of accurate experimental band intensities and a reasonable force field. While it will generally be assumed that these quantities are available, it should be noted that accurate band intensities are often difficult to obtain.³ Overlapping bands are particularly troublesome in this regard, and can lead to large uncertainties in measured intensities. This problem is considered in detail by Person and Steele.³

Since experiments cannot determine the sign of $\partial\mu/\partial Q_i$ (eq 2), the use of eq 5 leads to more than one possible set of $\partial\mu/\partial S_j$, depending on the choice of phase for $\partial\mu/\partial Q_i$. For a symmetry block with n modes, there will be 2^{n-1} possible sign combinations for $\{\partial\mu/\partial S_j\}$. One possible method of overcoming this problem lies in the use of ab initio intensity values. In the case of ethylene, ab initio methods agree with the experimental deuterium substitution results.⁶ Also, as will be seen below, Pulay's ab initio values for methane,⁷ ethane,⁸ and acetylene,⁸ when analyzed in terms of orbital rehybridization, are all consistent with chemical intuition.

Model treatments of infrared intensities are generally classified as zero-order or first-order theories. In zero-order

theory, the total dipole is written as a sum of k bond dipoles:³

$$\mu = \sum_k \mu_k \quad (8)$$

The dipole moment/coordinate derivative is then

$$\frac{\partial\mu}{\partial Q_i} = \sum_i \sum_k L_{ii}' \frac{\partial\mu_k}{\partial S_i'} \quad (9)$$

In cases where S_i' is a bending vibration, the $\partial\mu_k/\partial S_i'$ are pictured as arising from the geometric reorientation of the μ_k due to S_i' . Zero-order theory has been applied with little success to a number of molecules.⁹ In fact, it was found that different sets of μ_k were needed to describe different bending modes in the same molecule.⁹

The failure of zero-order theory is unfortunate, since such a model would fit well with chemical intuition and give some idea of the relative polarization of bonds. Clearly, molecular vibration must change the magnitudes of μ_k if eq 9 is to give nonzero values of $\partial\mu/\partial S_i'$ when S_i' is a bond stretch, since there is no geometric component. The results of zero-order theory suggest that this must also be true for bending modes. Inclusion of this effect characterizes first-order theory.³ This division into zero- and first-order theory was first proposed by Elyashevich and Wolkenshtein¹⁰ in the so-called "valence optical theory", and later improved by several authors.¹¹⁻¹³ Gribov's formulation¹¹ proves particularly useful. He writes μ as

$$\mu = \sum_k \mu_k \hat{e}_k \quad (10)$$

and

$$\frac{\partial\mu}{\partial Q_i} = \sum_i \sum_k L_{ii} \frac{\partial\mu_k}{\partial q_i} \hat{e}_k + \sum_i \sum_k \mu_k L_{ii} \frac{\partial\hat{e}_k}{\partial q_i} \quad (11)$$

where μ_k is the magnitude of μ_k and \hat{e}_k a unit direction vector along bond k . Such a formalism has been applied very successfully by Gribov to a large series of organic molecules.¹¹ Similar work by Orville-Thomas and co-workers¹⁴ has demonstrated the remarkable potential of this model. Group parameter sets (e.g., for CH_2 , CH_3) have been obtained from small molecules, then used to predict intensities for larger molecules.

The major drawback of Gribov's theory is that the $\partial\mu_k/\partial q_i$ are difficult to interpret. In the case of the typical olefinic deformation in Figure 1, terms like $\partial\mu_{\text{CH}_1}/\partial r_{\text{CH}_1}$ and $\partial\mu_{\text{CH}_1}/\partial r_{\text{CH}_2}$ are needed. No rationalization can be given for the relative magnitudes obtained for these parameters, so Gribov's theory reduces to parameter fitting.

An alternate form for $\partial\mu/\partial Q_i$ has been proposed by Decius.¹⁵ Starting with a μ of the form

$$\mu = \sum_j p_j \mathbf{z}_j \quad (12)$$

the $\partial\mu/\partial Q_i$ are then

$$\frac{\partial\mu}{\partial Q_i} = \sum_i \sum_j L_{ii}' \frac{\partial p_j}{\partial S_i'} \mathbf{z}_j + \sum_i \sum_j p_j L_{ii}' \frac{\partial \mathbf{z}_j}{\partial S_i'} \quad (13)$$

where p_j is the charge on atom j with direction vector \mathbf{z}_j , and the sum on j is over all atoms. In the limit of directly bonded (group) interactions, eq 13 contains no "cross" terms. For example, for the mode shown in Figure 1, only terms like $\partial p_{\text{H}_1}/\partial r_{\text{CH}_1}$ and $\partial p_{\text{C}}/\partial r_{\text{CH}_1}$ are needed. In most cases there will be fewer parameters in Decius' method than in Gribov's. Little work has been done using this method, although it should prove of much interest. As will be demonstrated below (section III), the Decius method can be considered a special case of Gribov's method.

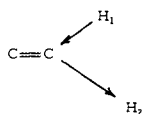


Figure 1. A typical olefinic deformation.

In an attempt to circumvent the problems of first-order theory, Morcillo et al. formulate the intensity problem in terms of atomic "polar tensors".¹⁶ The "polar tensor" for the α th atom is written as

$$P_X^{(\alpha)} = \begin{bmatrix} \partial\mu_x/\partial x_\alpha & \partial\mu_x/\partial y_\alpha & \partial\mu_x/\partial z_\alpha \\ \partial\mu_y/\partial x_\alpha & \partial\mu_y/\partial y_\alpha & \partial\mu_y/\partial z_\alpha \\ \partial\mu_z/\partial x_\alpha & \partial\mu_z/\partial y_\alpha & \partial\mu_z/\partial z_\alpha \end{bmatrix} \quad (14)$$

where μ_i is the i th component of the total dipole moment and x_α the x component of the α th atom. The total dipole change is then¹⁶

$$\Delta|\boldsymbol{\mu}| = \sum_\alpha P_X^{(\alpha)} X_\alpha \quad (15)$$

where X_α is the Cartesian displacement vector of the α th atom. The major advantage of the "polar tensor" method lies in the sum rules associated with it. Particularly, this method leads to the equation¹⁷

$$\sum_\alpha (1/m_\alpha)\xi_\alpha^2 = \sum_i A_i + \Omega \quad (16)$$

where m_α is the mass of the α th atom and Ω is a (known) correction arising from conservation of rotational angular momentum. Equation 16 has been used by King¹⁸ to obtain values for ξ_α , defined as the effective atomic charge, analogous to the p_j of Decius.

One problem shared by all of the theories mentioned above is that of the uniqueness of the parameters obtained. With such a large number of parameters fit to relatively crude experimental intensities, it would not be surprising if an incorrect set were obtained. Similar problems exist in the calculation of molecular force fields, where experimental positions are known much more accurately than intensities.²

Another problem lies in the determination of the absolute sign of the parameters, which would greatly assist any analysis. One way of obtaining the absolute sign is with quantum mechanical calculations of the intensity. While semiempirical methods have been used for this purpose, it has been noted that such methods cannot reproduce ab initio results.⁶ Pulay, however, has demonstrated the power of extended basis ab initio methods by calculating intensities for methane,⁷ ethane,⁸ ethylene,⁸ and acetylene.⁸ The agreement between experiment and theory for these calculations was very good, but little could be said about what chemically relevant factors are involved in molecular vibrations.

The problem of interpreting the ab initio results for ethylene has been considered by us,⁶ and a partial generalization in other molecules was also reported.¹⁹ In the present work, a full generalization of the theory based on orbital rehybridization is presented.

III. The Hybrid Orbital Rehybridization Model (HORM)

One possible way to reduce the numbers of parameters and obtain the correct set is to impose a physically motivated constraint on their ranges. As was done in the case of the hybrid orbital force field²⁰ (HOFF), orbital following provides such a constraint. In analogy with eq 11, one can write

$$\frac{\partial\boldsymbol{\mu}}{\partial Q_i} = \sum_t \sum_k \mu_k L_{ti}' \frac{\partial\hat{\mathbf{e}}_k}{\partial S_i'} + \sum_t \sum_k L_{ti}' \frac{\partial\mu_k}{\partial S_i'} \hat{\mathbf{e}}_k \quad (17)$$

Each $\partial\mu_k/\partial S_i'$ is rewritten as

$$\frac{\partial\mu_k}{\partial S_i'} = \frac{\partial\mu_k}{\partial\lambda_k} \frac{\partial\lambda_k}{\partial S_i'} \quad (18)$$

to give

$$\frac{\partial\boldsymbol{\mu}}{\partial S_i'} = \sum_k \mu_k \frac{\partial\hat{\mathbf{e}}_k}{\partial S_i'} + \sum_k \frac{\partial\mu_k}{\partial\lambda_k} \frac{\partial\lambda_k}{\partial S_i'} \hat{\mathbf{e}}_k \quad (19)$$

The $\{\lambda_k\}$ are the bond hybridization parameters defined by Coulson.²¹ A typical hybrid, $\phi(\lambda)$, is written as

$$\phi(\lambda) = (\phi_s + \lambda\phi_p)/(1 + \lambda^2)^{1/2} \quad (20)$$

with $\lambda = 1$ for an sp hybrid, $\sqrt{2}$ for sp², etc. Orbital orthogonality then requires

$$\lambda_i \lambda_k \cos \alpha_{ik} + 1 = 0 \quad (21)$$

where α_{ik} is the angle between the i, k hybrids.

The first term in eq 17 describes the intensity contribution resulting from a geometric reorientation of the μ_k , and will be referred to as the geometric component. The second term describes the change in μ_k due to orbital rehybridization, and thus will be called the rehybridization component.

A detailed analysis of eq 17 leads to many simplifications. The terms in $\partial\hat{\mathbf{e}}_k/\partial S_i'$ are easily calculated using the geometry and the constraint that rotational angular momentum is conserved.¹¹ The rehybridization terms present more of a problem. If S_i' is a bending coordinate, the $\partial\lambda_k/\partial S_i'$ are obtained explicitly by taking appropriate derivatives²⁰ of eq 21. Thus, the only parameters needed are the μ_k , $\partial\mu_k/\partial\lambda_k$, and $\partial\lambda_k/\partial S_i'$ (for S_i' a bond stretch). As will be shown in the next section, all of these parameters can be expressed as simple functions of the hybridization. Before considering their explicit evaluation, some qualitative features of the theory will be noted.

The intensities of certain bending modes can be expected to have essentially zero contributions from the rehybridization components. These modes are characterized by motions in which rehybridization would involve mixing in perpendicular p orbitals. Little rehybridization would be expected for this type of mode compared with modes not involving pure p orbitals.²² Classic examples of these modes are the H-C≡C bend in acetylene, the out-of-plane CH₂ bend in ethylene, and the out-of-plane CH bend in benzene. Other examples can easily be visualized. Bonds with λ 's appropriate to sp² or sp hybrids suggest the existence of orthogonal "pure p-like" orbitals. For example, the CH₂ group of cyclopropene has λ values characteristic of olefinic CH₂'s, while the olefinic CH's of cyclopropene act acetylenic. Thus the CH₂ wag or any olefinic CH bend in cyclopropene would be purely geometric, as will be seen below.

The assertion that such purely geometric modes exist clearly needs to be tested. Such tests, performed with ab initio wave functions, are reported in the following sections.

Before going into the details of the HORM method, another qualitative feature should be noted. Consider in particular the B_{3u} modes (S_{11} and S_{12} , Figures 2 and 3 and Table I) in ethylene. Motions of this symmetry allow for the formation of a carbon-carbon bond dipole. In the HORM, this $\mu_{C=C}$ is accounted for in the rehybridization component, while none of the other model theories can directly include this effect. As will be seen below, such "hidden" effects can be large, and are necessary for any comprehensive theory.

Finally, it should be pointed out that several vibrational modes cause intense vibrations simply because they reorient bonds with large bond moments. For example, the antisymmetric ($r_{13}-r_{23}$) stretch in cyclopropene (Figure 3) reorients the CH₂ group, giving rise to large dipole changes. Similar antisymmetric modes exist in such molecules as cyclopropane, bicyclobutane, and bicyclo[1.1.1]pentane. Ab initio calcula-

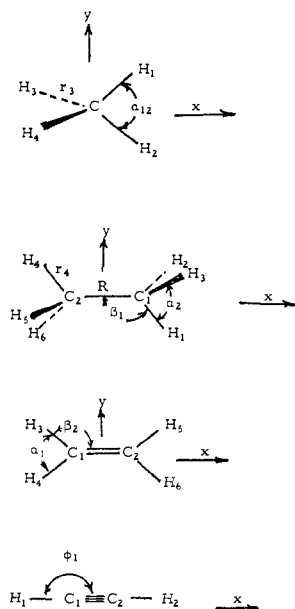


Figure 2. Molecular internal coordinates.

tions for this mode in cyclopropene are reported below.

If HORM is to be consistent with physical intuition, then there must be some simple relation between eq 10 and 11 and eq 12 and 13. In the limit that each μ_k can be replaced by two point dipoles on the terminal atoms, eq 10 can be rewritten as

$$\mu = \sum_k (q_k r_k) \hat{e}_k \quad (22)$$

where q_k is the charge associated with bond k , and r_k is the k th bond distance. Similarly, $\partial\mu/\partial S_i'$ becomes

$$\frac{\partial\mu}{\partial S_i'} = \sum_k r_k \frac{\partial q_k}{\partial S_i'} \hat{e}_k + \sum_k r_k q_k \frac{\partial \hat{e}_k}{\partial S_i'} \quad (23)$$

If the q_k which have a terminus on atom α are labeled q_k^α , the p_α can be written as

$$p_\alpha = \sum_k q_k^\alpha \quad (24)$$

Then, associating r_k with \hat{e}_k and noting that atoms i and j define bond k , one can write

$$\hat{e}_k r_k q_k = (\mathbf{z}_j - \mathbf{z}_i) q_k = \mathbf{z}_j q_k^j - \mathbf{z}_i q_k^i \quad (25)$$

since \hat{e}_k is the unit vector along r_k . With eq 24 and 25, it is clear that eq 11 gives eq 13.

The major assumption used in relating eq 11 to eq 13 was that the bond moments μ_k could be approximated by two charges, $+q_k$ and $-q_k$, separated by a distance r_k . As will be seen below and in Appendix A, this is only a crude approximation.

IV. Parameter Evaluation

The need to obtain absolute signs for $\partial\mu/\partial Q_i$ (and thus better experimental values for $\partial\mu/\partial S_j$) and to test the assumptions of the HORM can both be satisfied by accurate ab initio calculations. Pulay has demonstrated that extended basis ab initio calculations agree well with experimental values^{7,8} while we have considered the basis set dependence of ab initio intensities.⁶ The results are particularly relevant here, and will be briefly reviewed.

The results of ab initio calculations on ethylene showed that a 4-31G basis set augmented with CH and C=C bonding functions could quantitatively reproduce experimental intensities, while the 4-31G basis gave reasonable semiquantitative

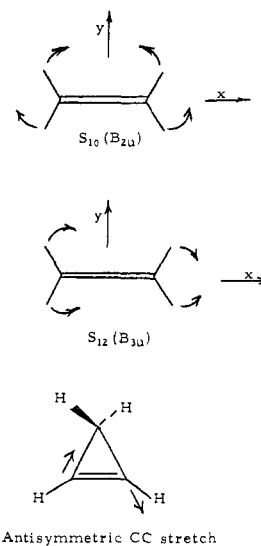


Figure 3. Selected vibrational modes.

agreement.⁶ Analysis of the Mulliken population shifts for the various internal modes in Table I indicated that the out-of-plane mode differed from the others in that its atomic charge shifts were essentially zero (i.e., $<10^{-4}$). This difference was interpreted to mean that the out-of-plane mode was due to the geometric reorientation of the CH₂ groups, while the other modes involved orbital rehybridization. Since this mode was due to purely geometric effects, a value of $\mu_{CH} = 0.74$ D (C-H⁺) could be obtained from the intensity. An examination of the effect of rehybridization for the in-plane modes also indicated that orbital rehybridization would change in such a way as to counteract the μ_{CH} dipole arising from geometric reorientation of the CH bonds.

The most important fact noted previously was that the out-of-plane mode intensity was essentially geometric in nature.⁶ On the basis of arguments in section III, it would thus be expected that the out-of-plane olefinic CH bends in cyclopropene and cyclobutene would show similar (small) charge shifts, as would the C≡C-H bend in acetylene. Ab initio calculations were performed (see below) on these modes, and gave essentially zero charge shifts. A more stringent test of this idea might be seen in the cases of propene, propyne, and 1,2-dimethylcyclopropene, where a CH₃ group could be bent out of the plane of the μ orbitals. Such calculations have been performed, and again, the charge shifts are essentially zero.

Localized molecular orbital (LMO) calculations have also been performed for the modes in Figure 2 and Table I, and are listed in Table II. Examination of this table clearly shows that the out-of-plane modes involve little rehybridization.

Another test of this "orthogonal orbital" idea would be in the calculation of charge shifts for the in-plane C=C-H bend in cyclopropene and CH₂ bend perpendicular to the plane bisecting C=C in cyclopropene. Since these CH bonds are roughly acetylenic and olefinic in terms of % s, there should be little charge shift. Ab initio calculations in these modes have been performed (see below) and confirm this expectation.

With these ideas in mind, one can begin to evaluate the necessary HORM parameters.

There are three sets of parameters which must be evaluated: $\{\mu_k\}$, $\{\partial\mu_k/\partial\lambda_k\}$, and $\{\partial\lambda_k/\partial r_k\}$. The $\{\mu_k\}$ can be obtained most easily from analysis of the purely geometric modes. In the symmetric molecules (Table I) ethylene (S_7) and acetylene (S_5), the necessary μ_k are just $\{\mu_{CH}\}$. The μ_{CH} associated with the 4-31G calculations above are listed in Table III, along with "experimental" values obtained from the experimental intensities. Also shown are the classical values for % s, experi-

Table I. Infrared-Active Symmetry Coordinate^a

Methane	
$S_{3a} = (r_1 + r_2 - r_3 - r_4)/2$	
$S_{4a} = (\alpha_{12} - \alpha_{34})/\sqrt{2}$	
Ethane	
$S_5 = (r_1 - r_2 - r_3 + r_4 + r_5 + r_6)/\sqrt{6}$	
$S_6 = (\beta_1 + \beta_2 + \beta_3 - \alpha_1 - \alpha_2 - \alpha_3 - \beta_4 - \beta_5 - \beta_6 + \alpha_4 + \alpha_5 + \alpha_6)/\sqrt{12}$	
$S_7 = (2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6)/\sqrt{12}$	
$S_8 = (2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6)/\sqrt{12}$	
$S_9 = (2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6)/\sqrt{12}$	
Ethylene	
$S_7 = (\delta_1 + \delta_2)/\sqrt{2}$	
$S_9 = (r_5 - r_6 + r_3 - r_4)/2$	
$S_{10} = (\beta_5 - \beta_6 + \beta_3 - \beta_4)/2$	
$S_{11} = (r_5 + r_6 - r_3 - r_4)/2$	
$S_{12} = (2\alpha_2 - \beta_5 - \beta_6 - 2\alpha_1 + \beta_3 + \beta_4)/\sqrt{12}$	
Acetylene	
$S_3 = (r_1 - r_2)/\sqrt{2}$	
$S_5 = (\phi_1 - \phi_2)/\sqrt{2}$	

Table II. LMO % s Values for Hydrocarbon Bends^a

Molecule	Mode ^b	Hydrogen	% s/100
C ₂ H ₂	GS ^c	<i>d</i>	0.5000
	S ₅	1	0.5000
C ₂ H ₄	GS	<i>d</i>	0.3678
	S ₇	<i>d</i>	0.3678
	S ₁₀	3	0.3635
	S ₁₀	4	0.3720
	S ₁₂	3	0.3602
	S ₁₂	5	0.3751
CH ₄	GS	<i>d</i>	0.2902
	S _{4a}	1	0.2836
	S _{4a}	3	0.2967

^a All angle displacements were 2°. ^b Defined in Table I. ^c Ground state, vibrationally unexcited value. ^d All hydrogens are equivalent.

mental values of the J_{13C-H} coupling constants, and the % s obtained from the J_{13C-H} using the observed linearity of J_{CH} and % s.²³

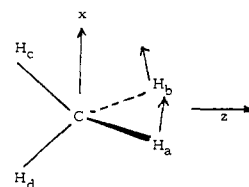
The experimental and 4-31G values (in the sense C-H⁺) of μ_{CH} appear to be related to the % s values and the NMR J_{13C-H} coupling constants for acetylene and ethylene. If this relationship were to hold for methane, then its μ_{CH} would be 0.55 D (the value in parentheses in Table III), while typical analyses of infrared intensities place it between 0.3 and 0.4 D.^{3,24} The origin of the difference lies in the neglect of the orbital rehybridization component in previous analysis. This effect is particularly important in symmetric hydrocarbons, where the intensity of modes other than the perpendicular ones described above depends strongly on the rehybridization component. As an example, consider the B_{2u} (S₁₀) mode in ethylene (Figure 3) with a 2° angle change. If $\Delta\mu$ is crudely written as


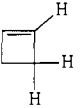
$$\Delta\mu = 2\mu_{CH}(\cos(\theta - 2) - \cos(\theta + 2)) \quad (26)$$

then $\mu_{CH} = 0.3$ D. However, rehybridization arguments suggest that a better form would be

$$\Delta\mu = 2(\mu_{CH} - \delta)\cos(\theta - 2) - 2(\mu_{CH} + \delta)\cos(\theta + 2) \quad (27)$$

where δ is the rehybridization moment.²⁵ For $\mu_{CH} = 0.74$ D (obtained from S₇), δ is found to be 0.013 D. Hence, a very small value for the rehybridization moment greatly affects the μ_{CH} obtained.

**Figure 4.** "Out-of-plane" mode in methane.**Table III.** μ_{CH} Values^a

Molecule	% s		J_{CH}	μ_{CH}			
	classi- cal	% s LMO		Exptl ^b	OOP, calcd ^c	LMO ^d	J_{CH} ^e
C ₂ H ₂	50	50	250	1.19 ^f	1.19 ^g	1.1	1.1
C ₂ H ₄	33	37	159	0.74	0.78 ^g	0.81	0.70
CH ₄	25	29	125	(0.55)	0.62 ^h	0.64	0.55
		46	220		1.02	1.02	0.97
		38	172		0.72	0.82	0.76
		40	170		0.88	0.88	0.75
		31	140		0.68	0.68	0.62

^a All values in D. ^b See text. ^c Calculated with 4-31G basis sets using out-of-plane bends and eq 34. ^d Equation 31. ^e Equation 32. ^f G. B. Mast and W. T. King, *J. Phys. Chem.*, 80, 2004 (1976). ^g Calculated with bond function basis sets, out-of-plane bends, and eq 34. ^h Calculated as described in text.

In order to obtain a true static μ_{CH} in methane, intensities for the mode in Figure 4 were calculated using 4-31G and 4-31G + bonding function basis sets. Examination of population changes for these calculations indicated that bonds labeled by H_a and H_b did not rehybridize, although H_c and H_d did. This is not surprising, since this is not a true "perpendicular" bend—in fact, orbital orthogonality couples all four bonds. Using these facts, two equations can be set up:

$$\Delta\mu_z = 2\mu_{CH} \cos(\alpha/2) \cos \beta - (\mu_{CH} - \delta) \cos(\alpha/2) - (\mu_{CH} + \delta) \cos(\alpha/2) \quad (28)$$

$$= 2\mu_{CH} \cos(\alpha/2)(\cos \beta - 1) \quad (29)$$

where β is the angle between the yz plane and the bisector of the H_aCH_b angle, α is the tetrahedral angle, and

$$\Delta\mu_x = 2\mu_{CH} \cos(\alpha/2) \sin \beta + (\mu_{CH} - \delta) \sin(\alpha/2) - (\mu_{CH} + \delta) \sin(\alpha/2) \quad (30)$$

Solving these equations for μ_{CH} and δ gives $\mu_{CH} = 0.85$ and 0.62 for 4-31G and 4-31G + bonding basis sets and $\delta = 0.010$ and 0.008 for a 2° change in β . Results on ethylene⁶ suggest that the bonding basis value is high by less than 0.1 D so μ_{CH} is between 0.5 and 0.62 D. If the linearity in Table III held true and $\mu_{CH} = 0.55$ D, then experimental values of $\partial\mu/\partial S$ and eq 30 gives $\delta = 0.007$ D. The coalescence of the ab initio and experimental values strongly suggests that $\mu_{CH} = 0.55$ D is reasonable, so this value will be taken as the "experimental" CH bond dipole in methane.

The appropriate linear relationships for the data in Table III are

$$\mu_{CH}^{\text{exp}} = 0.022(\% s) \quad (31)$$

$$\mu_{CH}^{\text{exp}} = 0.0044J_{CH} \quad (32)$$

$$J_{CH} = 5(\% s) \quad (33)$$

$$\mu_{CH}^{\text{exp}} = \mu_{CH}^{4-31G} - 0.25 \quad (34)$$

Table IV. C-C Moments

	μ_{tot} (exptl)	μ_{tot} 4-31G	% s ^a	$\mu_{\text{C-C}}$ (from expt)	$\mu_{\text{C-C}}^b$ (calcd)
	0.75 ^c	0.68	0.50	1.18	1.1
		0.864	0.44	0.81	0.84
	0.287 ^d	0.387	0.34	0.37	0.41
	0.364 ^e	0.34	0.33	0.32	0.35
	0.257 ^f	0.13	0.33	0.38	0.35
	0.083 ^g	0.06		0.06	0.04 ^h 0.11 ⁱ
	0.132 ^j	0.11		0.19 ⁱ	0.17 ⁱ
	0.190 ^k	0.118			0.22 ^l
	0.132 ^m	0.07			0.11 ^l
	0.45 ⁿ	0.54			-0.14 ^l

^aBased on J_{CH} . ^bCalculated from eq 31 and 40. ^cJ. S. Muentner and V. W. Laurie, *J. Chem. Phys.*, **45**, 855 (1966). ^dK. B. Wiberg, G. B. Ellison, J. J. Wendoloski, W. E. Pratt, and M. D. Harmony, manuscript in preparation. ^eD. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957). ^fT. N. Sarachman, *ibid.*, **49**, 3146 (1968). ^gD. R. Lide, Jr., *ibid.*, **33**, 1514 (1960). ^hLMO % s and eq 33. ⁱCalculations using eq 21 and 33. ^jR. D. Nelson, Jr., D. R. Lide, Jr., and A. B. Margott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 10 (1967). ^kS. S. Butcher and C. C. Costain, *J. Mol. Spectrosc.*, **15**, 40 (1963). ^lCalculated from experimental μ by subtracting μ_{CH} values. ^mH. Kim and W. D. Gwinn, *J. Chem. Phys.*, **42**, 3728 (1965). ⁿP. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *ibid.*, **30**, 512 (1959).

The observed dependence of μ_{CH} on a single parameter like % s is easily rationalized, although the original of this linear dependence is unclear. In the perfect pairing approximation, μ_{CH} for a CH bond along the z axis is written as

$$\mu_{\text{CH}} = [(\phi_s + \lambda\phi_p)/(1 + \lambda^2)^{1/2}] + b\phi_H \quad (35)$$

Relative to the bond center, μ_{CH} is thus

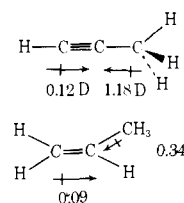
$$\mu_{\text{CH}} = z_C + b^2 z_H + \{[(\%s)(\%p) \times 10^{-4} z_{\text{sp}}]^{1/2} + 2b[(\%s) \times 10^{-2} z_{\text{s,H}}]^{1/2} + 2b[(\%p) \times 10^{-2} z_{\text{p,H}}]^{1/2}\} \quad (36)$$

where the definition % s = 100/(1 + λ^2) has been used and z_{ij} is the dipole moment contribution of orbitals i and j . The choice of bond center as origin guarantees that the total dipole will equal the sum of the bond dipoles, assuming that carbon contributes one nucleon to each CH bond. If r_{CH} is assumed fixed in all cases, then there is only one independent parameter in eq 36, since b can be eliminated by normalization and % s + % p = 100. The CH dipole can then be written as

$$\mu_{\text{CH}} = f(\%s) \quad (37)$$

The above derivation only justifies the fact that μ_{CH} is a function of % s. The suggested linearity of μ_{CH} with % s is not clearly contained in eq 36.

The relation between J_{CH} and % s²³ in eq 33 suggests that the intensity associated with certain bending modes in selected molecules should also be essentially geometric. For example,

Table V. 4-31G C-C Moments^a

^aCalculated from perpendicular bends, using μ_{CH} from Table III. See text.

the bridgehead CH bond in bicyclobutane and bicyclo[1.1.1]pentane are very much like acetylene CH bonds according to LMO analysis²⁶ or % s character obtained from J_{CH} .^{27,28} Similarly, the olefinic CH bonds in cyclopropene are acetylenic in terms of % s character.²⁹ This implies that, like acetylene, the CH bending will be purely geometric. As a test of this idea, μ_{CH} was calculated for the in-plane C-C-H bend of cyclopropene at the 4-31G level, giving $\mu_{\text{CH}} = 1.33$ D compared with $\mu_{\text{CH}} = 1.27$ D for the out-of-plane calculation. Similarly, the CH₂ groups in cyclopropene, bicyclobutane, and bicyclo[1.1.1]pentane are ethylenic, with a p orbital perpendicular to the plane of the CH₂ group. Values of μ_{CH} have been calculated at the 4-31G level for several molecules whose modes are described above, and are listed in Table III. The agreement between the various methods of calculating μ_{CH} is very good. Slight deviations are noted for the LMO (% s) values. This is due to the tendency of LMOs to overestimate the % s,³⁰ which arises because the LMO "carbon hybrids" cannot be truly orthogonal in the LCAO method.

The close agreement between μ_{CH} s predicted by eq 31, 32, and 34 offers reassurance that experimental μ_{CH} are quite accurate. Such a collection of μ_{CH} values offers many possibilities for obtaining C-C moments by vectorially subtracting out CH moments. The results of such calculations are summarized in Table IV.

In analogy with the CH bands, a perfect pairing two-electron wave function can be written for C-C bonds:

$$\phi_{\text{CC}} = \left(\frac{\phi_s^a + \lambda_a \phi_p^a}{(1 + \lambda_a^2)^{1/2}} + B \frac{\phi_s^b + \lambda_b \phi_p^b}{(1 + \lambda_b^2)^{1/2}} \right) \quad (38)$$

Here, ϕ_{CC} must contain two independent parameters, taken as % s_a and % s_b. Thus, μ_{CC} is written as

$$\mu_{\text{CC}} = f(\%s_a, \%s_b) \quad (39)$$

The simple linear relation

$$\mu_{\text{CC}} = 0.044(\%s_{\text{high}} - \%s_{\text{low}}) \quad (40)$$

fits the data in Table IV reasonably well. The sense of eq 40 is the positive sign on the carbon with lowest % s and the negative sign on the carbon with the highest % s.

The "experimental" value for propane is of particular interest. On the basis of the large (112°) CCC angle, C₂ would be expected to have more s character than C₁, so the C₁-C₂ dipole would have the negative sign on C₂. The "experimental" value reverses this, however, with $\mu_{\text{CC}} = 0.06$ D (C₁-C₂⁺). Ab initio LMO calculations using the experimental geometry agree with the experimental value in that % s₁ > % s₂²⁶ and $\mu_{\text{CC}} = 0.11$ D (C₁-C₂⁺). This can be seen as arising from the angular compression of the hydrogens on CH₃ (CCH = 111.2°)³¹ increasing the % s more than the C₁C₂C₃ opening at C₂. The signs of the experimental μ_{CC} in isobutane³² and 2-methylbicyclo[2.1.0]pentane³³ indicate similar behavior.

Ab initio values for μ_{CC} can be obtained in some cases by using the perpendicular orbital mode described above. Calculations at the 4-31G level were performed on propene, propyne, and 1,2-dimethylcyclopropene. The CH₃ groups in these

Table VI. HORM Bending Parameters

Molecule	Mode	Bond	% s ^a	($\partial\mu/\partial\lambda$) ^b exptl	-3.6×10^{-6} (% s) ³	($\partial\mu/\partial\lambda$) ^{b,c} calcd	Exptl/calcd	$8.2 \times 10^{-3} \times$ [(% s) ³ /(% p)] ^{1/2}
CH ₄	S _{4a}	CH	25.	-0.057	-0.056	-0.476	0.120	0.118
C ₂ H ₆	S ₆	CH	25.	(-0.053) ^d	-0.056	-0.476	0.111	
		CC	25.	-0.14	-0.112	-0.953	0.147	
		CH	25.	-0.045	-0.056	-0.476	0.095	
	S ₈	CH	25.	-0.061	-0.056	-0.476	0.128	
		CH	25.				Av 0.120	0.118
C ₂ H ₄	S ₁₀	CH	33.	-0.13	-0.129	-0.692	0.187	
	S ₁₂	CH	33.	(-0.13) ^d	-0.129	-0.692	0.188	
		CC, σ	33.	(-0.33) ^e	-0.258	-1.383	0.239	
		CC, π	33.	0.190				
						Av 0.205	0.190	

^a Classical values. ^b Units of D. ^c Equation 41 or 43 of text. ^d Calculated from eq 42; see text. ^e Calculated from eq 44; see text.

molecules were bent toward the π orbital. The overlap and charge shifts were small, on the order of the out-of-plane CH modes. These results, listed in Tables IV and V, are seen to be in good agreement with the geometrical values. The small magnitude of μ_{CC}^π disagrees with the suggestion of Pople³⁴ that most of the large magnitude of the propene dipole is due to deformation of the π cloud and confirms Dewar's speculation³⁵ that differences in the hybridization at C₂ and C₃ account for much of the total dipole moment. These results caution against the tendency to associate Mulliken population analysis charges with bond dipoles as was done with propene,³⁴ since no clear method is available for partitioning these charges into the bond dipoles.

As noted above, certain molecular deformations have large intensities because they geometrically reorient bonds which have large bond moments. An example of this is the antisymmetric ($r_{13}-r_{23}$) stretch in cyclopropane (Figure 3). The dipole moment changes for several values of this deformation were calculated at the 4-31G level. These dipole moment changes were the same as those obtained using μ_{CH} from Table III and assuming they arose from purely geometric bond reorientation. The CC stretches contribute little to the dipole changes, as would be expected for a bond with such low polarity (Table IV). Similar modes in other organic molecules should also give rise to large intensities, and thus be used to check infrared band assignments.

The experimental infrared intensities of methane, ethane, ethylene, and acetylene have been analyzed to obtain the rehybridization parameters. The geometric component for each mode was first eliminated using $\{\mu_{CH}\}$. All bending modes were then examined, and a set of $\partial\mu_k/\partial\lambda_k$ determined. The resulting $\partial\mu_k/\partial\lambda_k$ were then used to obtain $\partial\lambda_k/\partial r_k$ for the stretching modes. The complete set of parameters for bending modes is given in Table VI.

Examination of $\partial\mu_k/\partial\lambda_k$ as a function of % s shows a 3.6×10^{-6} (% s)³ dependence. This suggests that orbital following is incomplete by a factor of 8.2×10^{-3} (% s)/ λ for CH bonds,³⁶ since $\partial\mu_k/\partial\lambda_k$ can be obtained from eq 31 to give

$$\frac{\partial\mu_{CH}}{\partial\lambda_{CH}} = -4.4 \times 10^{-4} (\% s)^2 = -4.4 \times 10^{-4} [(\% s)^3 / (\% p)]^{1/2} \quad (41)$$

It then seems reasonable to associate the scale factor $8.2 \times 10^{-4} [(\% s)^3 / (\% p)]^{1/2}$ with the derivatives $\partial\lambda_{CH}/\partial S_j'$, since this quantity monitors the change in λ_k due to S_j' . Thus the effective ($\partial\lambda_k/\partial S_j'$) ($\partial\lambda_k^{\text{eff}}/\partial S_j'$) are written as:

$$\frac{\partial\lambda_k^{\text{eff}}}{\partial S_j'} = 8.2 \times 10^{-3} [(\% s)^3 / (\% p)]^{1/2} \frac{\partial\lambda_k^{100}}{\partial S_j'} \quad (42)$$

where 100 indicates the values based on complete orbital following.

It is important to point out a possible confusion in the definition of orbital following. As used here, orbital following is the change in % s character observed compared to that calculated using eq 31. A more usual definition might be to follow the vector direction of the p orbital vs. the vector direction of the CH orbital. However, the p orbital is not exactly collinear with the bond from LMO analysis.³⁷ Also, certain modes change % s character without changing the vector direction of the p orbitals (from the present LMO analysis, the B_{3u} bending mode of ethylene is an example).

Incomplete orbital following is, of course, not expected.³⁶ The scale factor $[(\% s)^3 / (\% p)]^{1/2}$ is consistent with classical electrostatic arguments—as % s increases (% p decreases), orbital directionality decreases, and an angular distortion thus requires less force. This force may be viewed as the electrostatic attraction between H and the bond electron cloud.

Note that no experimental values are given for the S₁₂ mode in ethylene or the S₆ mode in ethane. Since there are two values of $\partial\mu_k/\partial\lambda_k$ ($k = \text{CH}$ and CC), neither can be solved for directly. However, using eq 42, $\partial\mu_{CH}/\partial\lambda_{CH}$ can be obtained for the S₆ mode of ethane. On the basis of the CH results, it is suggested that $\partial\mu_{CC}/\partial\lambda_{CH}$ should be obtained by taking the derivative of eq 40 and scaling $\partial\lambda_{CC}/\partial S_j'$ by $[(\% s)^3 / (\% p)]^{1/2}$ as a scale factor. Using this method, the $\partial\lambda_{CC}/\partial S_j'$ is simply

$$\frac{\partial\mu_{CC}}{\partial\lambda_{CC}} = -8.8 \times 10^{-4} [(\% s)^3 (\% p)]^{1/2} \quad (43)$$

and the $\partial\lambda_{CC}/\partial S_j'$ are

$$\frac{\partial\lambda_{CC}^{\text{eff}}}{\partial S_j'} = 1.0 \times 10^{-3} [(\% s)^3 / (\% p)]^{1/2} \frac{\partial\lambda_{CC}^{100}}{\partial S_j'} \quad (44)$$

With the scale factor of $[(\% s)^3 / (\% p)]^{1/2}$, eq 43 and 44 give the correct values for ethane. As mentioned earlier, $\partial\mu_{C=C}/\partial\lambda_{C=C}$ in ethylene involves both σ and π shifts. If eq 44 is assumed to hold for the σ part of the mode, a value for $\partial\mu^{\pi_{C=C}}/\partial\lambda^{\pi_{C=C}}$ is obtained. Definition of a $\lambda^{\pi_{C=C}}$ is not physically realistic, but it serves as a useful parameter. The sense of $\Delta\mu^{\pi_{C=C}}$ is the same as the total dipole change while $\Delta\mu^{\sigma_{C=C}}$ is opposed. This suggests that the total dipole change is rehybridization controlled, giving a total net charge shift in the +x direction (Figure 3), while the π charge shifts to restore electrical neutrality. A similar effect is suggested by the s₁₁ mode in ethylene below.

It should be noted that the values of $\partial\mu_{CH}/\partial\lambda_{CH}$ obtained experimentally for the S₈ and S₉ mode of ethane are high and low compared with eq 42, averaging to the correct value. Part of the discrepancy can be attributed to the experimental superposition of the bands.⁸ However, it seems more likely that the degree of orbital following is slightly different in each of these modes.

Table VII. HORM Stretching Parameters

Molecule	Mode	Bond	$\partial\lambda/\partial r$	λ^2
CH ₄	S _{3a}	CH	2.62	3
C ₂ H ₆	S ₇	CH	2.73	3
C ₂ H ₄	S ₉	CH	0.90	2
	S ₁₁	CH	(0.90)	2
C ₂ H ₂	S ₃	CH	0.73	1

The corresponding analysis of the stretching modes presents more of a problem. A typical CH stretch might be expected to change the value of λ for carbon, along with the relative mixing coefficient for the carbon hybrid, hydrogen orbitals. Analysis based on charges shifts from Mulliken populations show that stretches transfer charge from carbon to hydrogen, with the reverse for compressions. Equation 35 and 36 still imply that a single parameter should be sufficient, however, so analysis will proceed as above.

The calculated HORM parameters are listed in Table VII. Values of $\partial\lambda/\partial r$ were first obtained from S_{3a} in methane, S₇ in ethane, and S₉ in ethylene. Since S₅ in acetylene allows a $\mu_{C\equiv C}$ to develop, a value for $\partial\lambda/\partial r$ could not be obtained directly for this mode. Using $\partial\lambda/\partial r$ from S₇, S₅ in ethane was analyzed to obtain the scale factor for $\partial\lambda^{\sigma_{CC}}/\partial S_5$, assuming the form

$$\frac{\partial\lambda_{CC}^{\sigma,eff}}{\partial S_5} = 1.0 \times 10^{-4}[(\% s)^3/(\% p)]^{1/2} \frac{\partial\lambda_{CC}^{\sigma,100}}{\partial S_5} \quad (45)$$

The small orbital following factor of $1.0 \times 10^{-4}[(\% s)^3/(\% p)]^{1/2}$ is reasonable, since S₅ does not directly involve the CC bond, only the CH bonds. Combining $\partial\lambda/\partial r$ from S₉ in ethylene and eq 45, the S₁₁ mode in ethylene was decomposed to give $\partial\lambda^{\sigma_{CC}}/\partial r$, which was then used to estimate $\partial\lambda/\partial r$ for the S₃ mode in acetylene. The increase of $\partial\lambda/\partial r$ with increasing p character is consistent with the arguments given above for orbital following, since λ should change more rapidly as the directionality increases. The acetylene and ethane values of $\partial\lambda/\partial r$ seem to suggest a rough λ^2 dependence. By this criteria, $\partial\lambda/\partial r$ for ethylene is low. This may be attributed to the counteracting effect of π cloud shifts mentioned above, which would give a value for $\partial\lambda/\partial r$ too small if the shifts moved so as to maintain electrical neutrality.

The results of the HORM analysis are listed in terms of the individual components of $\partial\mu/\partial S_j$ in Table VIII. It is clear from this table that the reorganization of the π cloud plays an important role in infrared intensities.

As was noted above, the HORM can be converted into a form analogous to the Decius¹⁵ equation. Using eq 22, values for the electron population on hydrogen and carbon can then

be determined from the HORM μ_{CH} and μ_{CC} . These values are tabulated in Table IX, along with values obtained using eq 16 and also ab initio Mulliken population values. There is a reasonable qualitative agreement among these values, supporting the expected relation between bond dipole moments and atomic populations. However, both the Mulliken population analysis and the effective charge calculations of King et al.^{17,18} assign methyl and vinyl hydrogens the same charge, while HORM assigns them a different charge. Chemical intuition (based on relative acidities or J_{CH} , for example) would predict that the charges should be different. An investigation of the relationship between the different methods of evaluating charges is needed.

The application of the HORM will subsequently be illustrated in connection with experimental studies of vibrational intensities in cyclopropene, cyclobutene, and related molecules.

V. Localized Molecular Orbital Analysis (LMO)





The sign and magnitude of $\mu_{CH}(C^{\ominus}H^{\oplus})$ obtained in these calculations disagrees with that usually calculated from LMO wave functions (2-3 D with $C^{\oplus}H^{\ominus}$).^{30,37} The assignment of a negative charge in H is physically unreasonable when compared with hydrocarbon acidities, and inconsistent with standard Mulliken population analysis, which assign H a charge of 0.1-0.2 esu. A more serious criticism of the $C^{\oplus}H^{\ominus}$ polarity is found in the calculation of dipole moment derivatives. For example, the calculated value for $\partial\mu/\partial S$ in the B_{2u} bending mode of ethylene at the STO-3G level is consistent only with $C^{\ominus}H^{\oplus}$, while LMO values obtained using the same STO-3G wave functions are reported as $C^{\oplus}H^{\ominus}$.³⁷ The problem with LMO bond moments arises because only one observable (μ) is unique in these calculations, while there is often more than one set of bond moments which is capable of reproducing μ (even when a series of similar molecules is used). A typical LMO bond moment analysis proceeds by calculating all electronic moments (μ_k) relative to a molecule fixed axis. Each bond moment is then transformed to its bond-centered axis assuming that the original molecule fixed moment corresponds to a point charge of 2e. While this method rigorously guarantees to give a set of μ_k which reproduce μ , the μ_k obtained are clearly inconsistent with chemical intuition. An alternative procedure can be seen by examining eq 36. According to this equation, each bond moment is described as a sum of point dipoles of fractional charges (given by the product of the appropriate expansion coefficients) at a point given by $z_{i,j}$. Conversion to a bond-centered origin involves individually converting all $z_{i,j}$. Bond moments calculated in this way are compared with the experimental values of the present work in Table X. The magnitudes of the LMO bond moments are in

Table VIII. HORM Contributions to $\partial\mu/\partial S^a$

Molecule	Mode ^b	$(\partial\mu/\partial S)_{total}$	$(\partial\mu/\partial S)_{geom}$	$(\partial\mu/\partial S)_{CH}$	$(\partial\mu/\partial S)_{CC,\sigma}$	$(\partial\mu/\partial S)_{CC,\pi}$
CH ₄	S _{3a}	0.833		0.833		
	S _{4a}	0.408	+0.635	-0.227		
C ₂ H ₆	S ₅	1.099		0.613	0.485	
	S ₆	0.223	0.898	0.075	-0.597	
	S ₇	1.227		1.227		
	S ₈	0.341	0.583	-0.242		
	S ₉	0.257	0.583	-0.326		
C ₂ H ₄	S ₇	1.050	1.050			
	S ₉	0.766		0.766		
	S ₁₀	0.093	0.740	-0.647		
	S ₁₁	0.606		0.442	0.237	-0.074
	S ₁₂	0.302	0.740	-0.187	-0.922	+0.672
C ₂ H ₂	S ₃	1.228		1.133	0.304	-0.209
	S ₅	1.482	1.482			

^a Values in D/Å. The phases of $\partial\mu/\partial S$ total have been assumed positive to facilitate comparison. ^b Coordinates from Table I and Figure 2.

Table IX. Atomic Charges Associated with HORM Parameters^a

Molecule	μ_{CH}	ρ_{HORM}^H	ρ_{HORM}^C	ρ_{4-31G}^H	$\rho_{eq\ 16}^H$	ρ_{4-31G}^C
C ₂ H ₂	1.1	0.77	6.23	0.70	0.60	6.30
C ₂ H ₄	0.73	0.85	6.30	0.84	0.82	6.32
CH ₄	0.55	0.89	6.48	0.85	0.83	6.60
	1.01	0.79	6.18	0.79		6.21
	0.84	0.83	6.38	0.85		6.32
	0.88	0.82	6.15	0.81		6.18
	0.68	0.86	6.28	0.84		6.33

^aCalculated using eq 22.

much better agreement with the present values than were the old LMO values.

In Appendix A, the difference between the two transformations is examined in detail, and it is found that the treatment of the two electrons as a point charge in the usual method is a poor (physical) approximation, since the electrons are spread over the bonding region. The success of the new method lies in the recognition of this fact by appropriately transforming the scaled atomic and bonding components of the bond dipole.

VI. Comparison with Bond Moments Obtained from Other Data

In the above, a self-consistent scheme for interpreting infrared intensities has been presented. It is now necessary to see if the results are consistent with other data. In the case of acetylene, a value of μ_{CH} has been estimated from infrared dispersion measurements and is 1.05 ± 0.02 D.³⁸ This is in excellent agreement with the value deduced from infrared intensities. The C-H bond dipole in benzene would be expected to be the same as for ethylene based on the similarity in % s character in the C-H bond, and based on the out-of-plane deformation mode, $\mu_{CH} = 0.73$ D for benzene.³⁹ The intermolecular forces between benzene molecules in the solid phase have been studied, and in order to fit both high-pressure and low-pressure data, it was necessary to assume a $\mu_{CH} = 0.83$ D.⁴⁰ This is subject to some error because of the nature of the parameter fitting. However, the large value clearly shows that the value deduced from infrared intensities has a reasonable magnitude. In the case of methane, the μ_{CH} derived from the antisymmetric bending mode must be a lower limit. Again, in fitting structural data by the molecular mechanics method, a $\mu_{CH} = 0.5$ D for methylene C-H bonds was needed.⁴¹ This is in good agreement with the value $\mu_{CH} = 0.55$ D obtained here. It is clear that the μ_{CH} values derived from infrared intensities are physically meaningful quantities.

Appendix A

In this appendix, the relation between the two LMO transformations described in section V is developed. In the usual LMO method, μ is written as the sum of localized bond dipoles:

$$\mu = \sum_{k=1}^n \mu_k \quad (\text{A-1})$$

Each μ_k is taken as a sum of an electronic moment z_{el} (times -2 for two electrons) and a nuclear term composed of one nucleon from each bond center. Where k labels bond AB, this gives

$$\mu = \sum_k (-2z_{el}^k + z_A^k + z_B^k) \quad (\text{A-2})$$

As written in eq A-2, all z_{el}^k are relative to the same molecular

Table X. LMO Values for μ_{CH} ^a

Molecule	μ_{CH}	
	LMO	Exptl
CH ₄	0.82	0.55
C ₂ H ₄	0.93	0.74
C ₂ H ₂	1.02	1.10

^aCalculated as described in text. Values in D. The direction of the bond dipoles was C⁻-H⁺ in all cases.

origin. In order to transform the k th bond to an origin at the k th bond center, the electronic component of eq A-2 is viewed as consisting of two point electrons at position z_{el}^k . The position z_{el}^k is then transformed to the k th bond center, and so on for the remaining bonds. In this way, each μ_k has the same projection on all axes and μ is conserved in a bond moment fashion.

There is, however, another transformation which conserves μ , but on a molecular basis. This other method arises because a typical AB bond

$$\Phi_{AB} = a\phi_A + b\phi_B \quad (\text{A-3})$$

has a dipole moment

$$\mu_{AB} = -2(a^2z_{A,A} + b^2z_{B,B} + 2abz_{AB} + z_A + z_B) \quad (\text{A-4})$$

where z_{ij} is the i,j th matrix element of z . The most direct way to transform this equation is to transform each z_{ij} individually. To do this, the bond center coordinate ($= (z_A + z_B)/2$) is subtracted from z_{ij} to give

$$\mu_{el, bond}^{A,B} = -2\{a^2[z_{A,A} - (z_A + z_B)/2] + b^2[z_{B,B} - (z_A + z_B)/2] + 2ab[z_{A,B} - (z_A + z_B)/2]\} \quad (\text{A-5})$$

Rearranging gives

$$\mu_{el, bond}^{A,B} = -2\{a^2z_{A,A} + b^2z_{B,B} + 2abz_{AB}\} + \{(a^2 + b^2)(z_A + z_B) + 2ab(z_A + z_B)\} \quad (\text{A-6})$$

If μ is to be conserved bond by bond, the second term in eq A-6 must give $(z_A + z_B)$ (to reproduce eq A-4). Since $a^2 + b^2 \approx 1$ by normalization, this condition is not satisfied owing to the $2ab(z_A + z_B)$ term. However, a molecular origin can easily be chosen so that the sum of μ over all n bonds equals the sum of terms like the second term in eq A-6.

Using $\Delta_{AB} = (z_A + z_B)/2$ for the bond center position, the extra term is just $4ab\Delta_{AB}$. It is this additional term which differentiates the new LMO method from the old. The significance of this term can be understood in the following way. Since the electron density of a localized bond orbital is spread over a large region of space, replacing it by the two electrons at a single point is a poor (physical) approximation. A better guess would be to approximate it as a scaled atomic charge (i.e., the a^2 and b^2 terms) and a scaled overlap charge (the ab terms). It is essentially the averaging out of this overlap moment that causes the usual LMO method to fail.

It is important to note that choice of a particular molecular origin is just a mathematical artifact used to define the transformation. Once the bond moments are obtained they are free of this choice. For the molecules treated here, where the origin is the geometric center, μ is conserved automatically. If nonsymmetric molecules are considered, it is interesting to note that the appropriate origin is roughly just the geometric center of all bond centers.

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Basis Set and Electron Correlation Effects on the Total Electron Density in H₂O, H₂S, and BH

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Abstract: The effects of basis set variation and inclusion of electron correlation in ab initio calculations of molecular electronic structure are studied. The ground states of H₂O, H₂S, and BH at their experimental gas phase geometries are chosen for systematic sets of detailed computations using Slater orbital basis sets and ranging in complexity from minimum basis sets to near Hartree-Fock with configuration interaction. Total electron density maps are obtained for each molecule, at each level of approximation, for all planes of interest, and difference density plots are calculated and discussed.

Introduction

Electron density maps have been used for many years to visualize electron distributions in molecules.¹ They have considerably sharpened the chemist's intuition, since a visual representation of electron density can yield information and draw attention to effects otherwise not fully appreciated by examination of a cumbersome set of numbers, such as a wave function or a density matrix.

The most common types of distribution maps used previously are orbital wave function, orbital and total density, and atomic and ionic difference density plots. The latter are supposed to show the changes in electron distribution as atoms or ions are brought together to form the molecular system. Although these maps have contributed considerably to our understanding of chemical bonding, they have been marred by the arbitrariness of the atomic or ionic states used. This situation arises because atoms in molecules are best viewed as modified to some degree,² thus creating an ambiguity as to

which type of atomic density is the most relevant. Individual orbital density plots, though also quite helpful, suffer from the fact that the same total electron distribution can be partitioned among orbitals in a multitude of ways, the grounds for a given selection being convenience in the study of some chemical or physical property.

Total electron densities, however, are directly related to experiment, and are free from the aforementioned arbitrariness and ambiguities. Hence, they are more relevant for a broad general study intended to analyze the geographical properties of the electron distribution itself, rather than a particular molecular property which depends on it.

Theoretical electron distributions are known to be highly sensitive to the basis set used to expand the molecular wave functions, and in addition electron correlation makes a second-order contribution to the ground-state one-electron density function of a closed-shell molecule. Consideration of these two types of dependences can aid in understanding and interpreting many features of chemical bonding, as well as the variation of