

Infrared Band Intensities, Electric Charge Distribution in Molecules and Polar Properties of Valence Bonds

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The possibility of deriving information on the charge distribution in molecules *via* transformation of vibrational intensities in the infrared spectra is discussed. Dynamic polar properties of the valence bonds can be characterized by empirical parameters, termed bond polar parameters, evaluated from experimental IR intensities. The theoretical prerequisites of the bond polar parameter method and some applications are discussed.

INTRODUCTION

The vibrations of a molecule can be associated with stretchings and bendings of the constituent valence bonds. Thus vibrational spectroscopy provides accessible experimental means to study properties of individual bonds. Comprehensive analysis of the vibrational frequencies by the normal coordinate method results in determination of the potential force field, and its parameters — the force constants — are considered as useful experimental characteristics of the intramolecular forces. The intensities of the infrared bands are related to the dipole moment changes accompanying vibrational motion. Hence, infrared band intensities are directly dependent on the electric charge distribution in molecules and its dynamics. As in the case of the frequencies the charge fluctuations accompanying vibrational distortions may, in principle, be associated with the changes in length and orientation of separate bonds. IR intensity theories are used in decomposing the experimental integrated band intensities into quantities characterizing polar properties of simple molecular sub-units.

The development of a physically well-founded model of intensities necessitates detailed understanding of the factors determining the dipole moment changes with vibrational distortions. Such information has become available as result of quantum-mechanical calculations on vibrational properties of molecules carried out mainly during the past fifteen years (see *e. g.* Refs. 1—10). The theoretical determination of the main parameters of the infrared spectra — frequencies and intensities — has become an important test for the credibility of any new or improved quantum-mechanical method. The evaluation of these quantities is, on one side, relatively easy, while the results provide, on the other, criteria for the accuracy of the two possibly most important characteristics that come from molecular orbital calculations: the

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energy and the charge distribution as reflected in the computed frequencies and intensities.

In this paper we review results from quantum-mechanical calculations that shed light on the intramolecular effects accompanying vibrational distortions and the factors determining the band intensities in infrared spectra. These results have formed the theoretical basis for the development of parametric model of IR intensities recently proposed.^{11,12} Brief description of the method is given, and its application in interpreting the gas-phase infrared intensities of the four methyl halides discussed.

CHARGE DISTRIBUTION AND IR BAND INTENSITIES

The integrated intensity of an infrared absorption band is proportional to the square of the transition moment $\sum_i |\langle i+1 | \hat{p} | i \rangle|^{13}$

$$A_i = \frac{8 \pi^2 N_0 \nu_i}{3 h c (4 \pi \epsilon_0)} \sum_i |\langle i+1 | \hat{p} | i \rangle|^2 \quad (1)$$

where ν_i is the observed frequency of the vibration, N_0 — the Avogadro number, h — the Planck constant, and ϵ_0 — the permittivity of free space. Experimental IR band intensities are usually interpreted in terms of dipole derivatives with respect to various types of vibrational coordinates. Under the assumption of electrical and mechanical harmonicity A_i is transformed into dipole moment derivative with respect to normal coordinate, Q_i , by the relation

$$A_i = \frac{N_0 \pi g_i}{3 c^2 (4 \pi \epsilon_0)} \frac{\nu_i}{\omega_i} \left(\frac{\partial p}{\partial Q_i} \right)^2 \quad (2)$$

with

$$\left(\frac{\partial p}{\partial Q_i} \right)^2 = \left(\frac{\partial p_x}{\partial Q_i} \right)^2 + \left(\frac{\partial p_y}{\partial Q_i} \right)^2 + \left(\frac{\partial p_z}{\partial Q_i} \right)^2$$

In expression (2) g_i is the degeneracy of the i -th vibration and ω_i — the harmonic frequency. Note that only the absolute magnitude of $\partial p / \partial Q_i$ can be determined from the experimental intensity values. In the following parts we shall discuss the intramolecular charge reorganizations contributing to the matrix element $\sum_i |\langle i+1 | \hat{p} | i \rangle|$.

LCAO MO Expression of Dipole Moment Contributions Determining IR Band Intensities

In the framework of the LCAO MO approach the Cartesian component of the dipole moment for a closed shell molecule described by a single determinantal wave function may be written as^{4,7}

$$p_x = -e \sum_{\Lambda} \sum_{\nu}^{\Lambda} (P_{\nu\nu} F_{\nu\nu} - X_{\Lambda} Z_{\Lambda}) - e \sum_{\Lambda \neq B} \sum_{\mu}^{\Lambda} \sum_{\nu}^B P_{\mu\nu} F_{\mu\nu} - e \sum_{\Lambda} \sum_{\mu \neq \nu}^{\Lambda} P_{\mu\nu} F_{\mu\nu} \quad (3)$$

with

$$F_{\mu\nu} = \langle \Phi_{\mu} | x | \Phi_{\nu} \rangle, \quad (4)$$

and

$$P_{\mu\nu} = 2 \sum_{s(\text{occ})} c_{\mu s} c_{\nu s} \quad (5)$$

where $\phi_{\mu,\nu}$ are atomic orbitals, and $P_{\mu\nu}$ — element of the electron density matrix, expressed in the usual notation. X_A and Z_A are the Cartesian coordinate and the charge of A-th nucleus. Expression (3) provides a convenient interpretation of the molecular dipole moment in terms of contributions associated with the constituent atoms and their orbitals.

The first term in Eq. (3) defines the contribution to the molecular moment from the net charges assigned to the atoms. It can be regarded as a point charge contribution provided that the basis set consists of orbitals symmetrical with respect to the nuclei (pure *s*, *p*, *d* orbitals). This term is denoted by p_q . The second term gives a measure of the contribution to the dipole moment arising from the overlap density of orbitals on different atoms, usually referred to as the homopolar moment, p_r . The third term is the hybridization moment, p_η .

For molecular vibration, described by a normal coordinate Q_i , all three terms may change. Thus

$$\begin{aligned} \frac{\partial p}{\partial Q_i} = & \frac{\partial}{\partial Q_i} \left\{ -e \sum_A \left(\sum_\nu P_{\nu\nu} F_{\nu\nu} - X_A Z_A \right) \right\} + \frac{\partial}{\partial Q_i} \left\{ -e \sum_{A \neq B} \sum_\mu \sum_\nu P_{\mu\nu} F_{\mu\nu} \right\} \\ & + \frac{\partial}{\partial Q_i} \left\{ -e \sum_A \sum_{\mu \neq \nu} P_{\mu\nu} F_{\mu\nu} \right\} \end{aligned} \quad (6)$$

Contributions from these three terms to the dipole changes determining IR band intensities will be considered in more detail.

Atomic Point Charge Term

The first term in Eq. (3) may rigorously be related to bond moments. Therefore the corresponding dipole contributions to the $\partial p/\partial Q_i$ gradients are correctly described by the bond moment approximation, implicit in some infrared intensity theories. With the aid of MO calculations Bruns and Person¹⁴ have shown that a substantial amount of electronic charge may be transferred between the atoms as the molecule vibrates. The contribution to the overall dipole moment variation due to the atomic charge terms may, therefore, be divided into two parts. Firstly, the change in p during vibration due to the motion of the equilibrium charges, p_{qe} , and, secondly, changes in p due to the flow of electronic charge induced by the vibrational motion. These two terms may be expressed as follows

$$p_{qe} = -e \sum_A \sum_\mu P_{\mu\mu} (F'_{\mu\mu} - F_{\mu\mu}) \quad (7)$$

$$p_{\Delta q} = -e \sum_A \sum_\mu (P'_{\mu\mu} - P_{\mu\mu}) F'_{\mu\mu} \quad (8)$$

The superscript ($'$) denotes that the associated term refers to the molecule in a distorted geometry, while the absence of prime indicates that the term refers to molecule in its equilibrium geometry.

The appearance of a charge flux term does not contradict the bond moment description of the molecular dipole moment but the corresponding bond moment fluctuations have to be taken into account.

Homopolar Term

The second term in Eq. (3) arises from the overlap density of orbitals on different atoms. As in the former case, the corresponding dipole changes induced by vibrational distortions can be expressed as

$$p_{\sigma\sigma} = -e \sum_{A \neq B} \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu} (F'_{\mu\nu} - F_{\mu\nu}) \quad (9)$$

$$p_{\Delta\sigma} = -e \sum_{A \neq B} \sum_{\mu}^A \sum_{\nu}^B (P'_{\mu\nu} - P_{\mu\nu}) F'_{\mu\nu} \quad (10)$$

These dipole terms cannot immediately be associated with bond moments since $P_{\mu\nu}$ and $F_{\mu\nu}$ are taken over all pairs of atoms in a molecule. It may, however, be argued that the dipole integrals between bonded atoms make the greater contribution to the homopolar dipole term. Thus, in a kind of a 'tight-binding approximation' the bond moment representation still retains certain merits as far as this dipole term is concerned.

Hybridization Term

The last term in Eq. (3) can also be split into a part representing the change in p arising from distortions of equilibrium charges, and a part determined by charge density fluctuations.

$$p_{\eta e} = -e \sum_A \sum_{\mu \neq \nu}^A P_{\mu\nu} (F'_{\mu\nu} - F_{\mu\nu}) \quad (11)$$

$$p_{\Delta\eta} = -e \sum_A \sum_{\mu \neq \nu}^A (P'_{\mu\nu} - P_{\mu\nu}) F'_{\mu\nu} \quad (12)$$

Even at equilibrium p_{η} is not formed by bond directed partial moments. Neither can one predict the change of magnitude and direction of these atomic dipoles during vibrations. Therefore, the expression of p_{η} in term of bond moments seems little justified. The role of the atomic dipoles in determining IR band intensities can most easily be visualized by the contribution of lone pair moments to the dipole change associated with a given vibration. Smit and Van Dam¹⁵ have shown with the aid of large basis set *ab initio* MO calculations that dipole moment derivatives associated with lone-pair moments make a substantial contribution to the overall dipole derivatives in the case of the ammonia molecule. In the framework of the bond moment description the lone-pair moment contribution is implicitly included in the dipole contributions arising from distortions of the adjacent bonds.

The contributions of the charge reorganization terms to the dipole moment changes induced by vibrational distortions may be quite considerable. The relative importance of the various composite dipole terms is illustrated by molecular orbital calculations of the contributions of $p_{\Delta q}$, $p_{\Delta\sigma}$ and $p_{\Delta\eta}$ to the dipole moment derivatives with respect to symmetry coordinate for the IR-active bending vibration of methane⁷ (Table I). The following basis sets have been used: (1) Minimal Slater basis with exponents taken from Ref. 16. Each Slater orbital is expanded as 4 GTO/STO according to the data of Stewart.¹⁷ (2) Double zeta (DZ) Slater basis with exponents given by Clementi¹⁸ expanded as 4 GTO/STO. (3) Dunning *sp* contracted gaussian set.¹⁹ (4) A set of »well-

TABLE I
Contributions of the Charge Reorganization Terms to $\partial p/\partial S_{4a}$ Dipole Moment Derivative in Methane^a

Sign choice $\partial p/\partial S_{4a}$	Experimental/D rad ⁻¹ ^b			
	++	--	+-	--
	0.408	-0.408	-0.371	0.371
Theoretical/D rad ⁻¹				
Basis set	$\partial p/\partial S_{4a}$	$\partial p_{\Delta q}/\partial S_{4a}$	$\partial p_{\Delta\sigma}/\partial S_{4a}$	$\partial p_{\Delta\eta}/\partial S_{4a}$
(1)	-1.779	0.321	0.103	-0.446
(2)	-0.798	0.521	-0.014	-0.684
(3)	-0.551	0.259	-0.380	0.419
(4)	-0.659	0.325	-0.896	0.778
(5)	-0.571	0.555	-0.544	0.442
(6)	-0.216	0.514	-0.390	-0.445
(7)	-0.550	0.215	0.097	-0.634
(8)	-0.261	0.294	0	-0.435
(9)	-0.021	0.319	0	-0.393

^a For molecular geometry data, definition of cartesian reference system, internal and symmetry coordinate, see Ref. 63.

^b Unscaled by equilibrium bond length symmetry coordinate S_{4a} is used.

^c Sign choice for $\partial p/\partial Q_i$ derivatives.

-balanced« uncontracted s and p gaussians.²⁰ (5) A set of contracted gaussians²¹ including polarization functions.²² (6) A double zeta plus polarization (DZ + P) Slater basis, expanded as for basis (1). (7) The CNDO/2 method. (8) The INDO method. The theoretical values for $\partial p/\partial S_{4a}$ are compared with the experimental dipole derivative. The last column in Table I contains the partial dipole gradients arising from the atomic dipole term. As can be seen all MO methods used predict large contributions from the charge reorganizations associated with the atomic dipoles.

The data presented in Table I reveal also the strong dependence of the theoretical dipole gradients on the basis set used. It is not the subject of the present paper to survey quantum mechanical calculations of dipole moment derivatives, continuously reported by many research groups. It is necessary to point out, however, that theoretical estimates of the dipole moment gradients proved extremely valuable in determining the sign of these quantities. As is known, only absolute values can be determined from the experimental intensities (Eq. 2). As is seen (Table I) the various basis set calculations predict a negative sign for the $\partial p/\partial S_{4a}$ derivative in methane. In these days of fast development of computational science the objectives of researchers are much higher — viz. reliable theoretical predictions of the magnitude of dipole moment derivatives, resp. IR intensities become feasible. Here we are tempted to adduce just an example — the results from recent *ab initio* MO calculations using 6-31G** basis set on some simple hydrocarbons reported by Wiberg and

Wendoloski²³. In Table II the experimental and theoretical dipole derivatives with respect to the symmetry coordinates for ethylene and acetylene are shown. Considering the errors involved in the evaluation of the experimental quantities the agreement between the two sets is very satisfactory indeed.

TABLE II
Experimental and Theoretical $\partial p/\partial S_j$ Derivatives for Ethylene and Acetylene as Reported by Wiberg and Wendoloski (Ref. 23)

Vibration		Observed	$ \partial p/\partial S_j ^{a,b}$ Calculated ^c
Ethylene			
B_{1u}	7	1.05	1.14
B_{2u}	9	0.80	0.91
	10	0.09	0.08
B_{3u}	11	0.63	0.74
	12	0.30	0.25
Acetylene			
u	3	1.26	1.42
u	5	1.49	1.56

^a In units D Å⁻¹ and D rad⁻¹.

^b For the sources of experimental data, see Ref. 23.

^c Using 6—31 G** basis set.

Electron Density Function and Infrared Intensities

An alternative interpretation of the intramolecular factors determining the dipole moment changes associated with vibrational motion may be based on considerations involving the electron charge density function, the spatial part of which is an observable physical quantity. The function $\rho(\mathbf{R})$ defining the electron density at position \mathbf{R} in LCAO expansion reads

$$\rho(\mathbf{R}) = \sum_{\mu,\nu} P_{\mu\nu} \Phi_{\mu}(\mathbf{R}) \Phi_{\nu}(\mathbf{R}) \quad (13)$$

$P_{\mu\nu}$ are elements of the charge density matrix, and $S_{\mu\nu}$ — overlap integrals over basis set atomic orbitals. Integration of $\rho(\mathbf{R})$ over the entire molecular space gives the number of electrons in a molecule. It is possible in principle to partition the molecular space into sub-spaces related to the constituent atoms, and to integrate $\rho(\mathbf{R})$ over these sub-spaces. As result, estimates of the charges associated with individual atomic sites are obtained. If the atomic sub-spaces are considered as points in the molecular space we arrive at a point-charge model of the molecule. There is a continuing argument as to the best way of partitioning the electron charge density and the definition of formal atomic charges.²³⁻²⁸

We have seen that static and dynamic dipoles contribute to the dipole moment variations determining IR band intensities. A particular difficulty in

a point-charge description of IR intensities arises from the necessity to consider, one way or another, the various charge reorganizations, different for each vibration in a molecule. As a consequence, the point-charge approach applied to the theory of vibrational intensities leads to parametric models in which the number of molecular parameters to be determined exceeds by far the number of independent experimental observables. To make the inverse intensity problem solvable additional approximations and constraints have to be imposed. In this respect other molecular properties related more closely to the equilibrium charge distribution have, evidently, better chances to be qualitatively or semiquantitatively described using the point-charge model. Thus, in a recent paper Maksić and Rupnik³⁰ have shown that the point-charge approach employed in the framework of semiempirical MO theories provides satisfactory interpretation of ESCA chemical shifts, diamagnetic shielding of nuclei, and of the diamagnetic part of molecular magnetic susceptibility. Returning to the charge density description of the intramolecular factors determining IR intensities we would like to discuss, in brief, particularly interesting results reported recently by Wiberg and Wendoloski.^{23,31} In their studies special attention is focussed on the definition of formal atomic charges. The molecular space is divided into sub-spaces in such a way that the atomic charges obtained after integration are physically close to the corresponding quantities derived from experimental infrared intensities. Band intensities for several simple molecules associated with vibrations of M—H bonds (M = C, Si, N) are analysed with the aid of 6-31G** MO calculations. The results show that, at equilibrium, the hydrogen charges are negative in all hydrocarbons studied, except for the case of the acidic hydrogen in acetylene. Point-charge interpretation of the experimental IR intensities of the bending modes in these molecules leads to the following values for the effective bond moments: $\mu_{\text{CH}}^{\text{eff}} = 0.74 \text{ D (C}^- \text{—H}^+)$ in ethylene, $\mu_{\text{CH}}^{\text{eff}} = 1.19 \text{ D (C}^- \text{—H}^+)$ in acetylene, and $\mu_{\text{CH}}^{\text{eff}} = 0.55 \text{ D (C}^- \text{—H}^+)$ in methane, in obvious disagreement with the calculated equilibrium charges. The authors have shown that this discrepancy is due to incomplete orbital following in the bending motion, which leads to the formation of bent bonds. From the analysis of the intramolecular charge reorganizations based on theoretical investigation of the electron charge densities Wiberg and Wendoloski conclude that IR intensities are determined by: (1) Motion of static bond moments; (2) Creation of a bent bond moment arising from incomplete orbital following; (3) Changes in bond moments due to rehybridization.

In these studies no example of molecule with lone-pair of electrons is considered. It may be expected that in such cases other factors would also interfere.

Generalizing, two different approaches — the first based on analysis of the contributions of the LCAO composite dipole terms, and the second, based on studies of properties of the electron charge density function — reveal a complex picture of intramolecular electronic effects determining band intensities in infrared spectra. The application of the point-charge approach in describing this particular molecular property is not straightforward. Special care has to be taken in order to account for the various charge fluctuations accompanying vibrational motion.

Derivatives of the Total Dipole Moment as Infrared Intensity Parameters

The interpretation of IR band intensities in most current studies is based on theoretical approaches involving the point-charge model. This is determined by the fact that the intensity parameters obtained are expected to provide experimental information about the equilibrium charge distribution, which, as nicely described by Person², may be regarded as the chemistry of an isolated molecule. Particularly useful in this respect have proved the valence-optical theory³²⁻³⁴, its extensions and modifications³⁵⁻³⁷. As we have seen, however, the exact physical significance of intensity parameters derived using the point-charge approach is far from clear because of the complexity of intramolecular charge reorganizations accompanying vibrational motion.

Alternative approaches for interpretation of infrared band intensities are based on models employing as parameters derivatives of the total dipole moment^{11,12,38-40}. The point-charge (bond moment) approximation is avoided, and as additional advantage, the number of independent intensity parameters equals the number of experimental observables. The atomic polar tensor theory^{38,39} which transforms IR intensities into derivatives of the total dipole moment with respect to atomic cartesian displacements has found considerable application in studies in this field, especially during the past decade.³

Chemical bonds are the most basic structural elements reflecting the transition from isolated atoms to molecules. It seemed worthwhile to seek an alternative approach for interpretation of the intensities in the infrared spectra using as parameters quantities characterizing individual valence bonds, while avoiding the bond moment approximation.

Since the aim is to evaluate intensity parameters characterizing properties of valence bonds it is particularly important to determine to what extent quantities representing derivatives of the total molecular moment can be related to the local bond polar properties. On the experimental side comparisons of parameters for different molecules may shed light on this question. Taking into account, however, the various difficulties implicit in intensity analysis, for example the accuracy of measurements, the accuracy of force field, the sign ambiguity for the dipole gradients, it becomes clear that direct answer from experimental data is not easy to obtain. On the other hand MO calculation can provide extensive and reliable information in this respect. Here we shall briefly review some of the results obtained.⁴¹⁻⁴⁵

Transferability of intensity parameters is considered to indicate clearly the extent to which these quantities are related to local structural features. With the aim of analysing the transferability of intensity parameters associated with C—H bonds molecular orbital calculations of dipole moment derivatives related to vibrations of the methyl group in a series of normal paraffins and their fluoro and nitro derivatives were carried out.^{42,45} In order to include larger molecules the semiempirical CNDO/2 method was used. It should be emphasized that in these studies we are interested in trends of changes and relative magnitude of intensity parameters, whilst the absolute numerical values are less important. For such purposes the valence electron semiempirical methods have proved reliable. In Table III dipole moment derivatives associated with the methyl symmetric stretching and deformation vibrations for the C₂—C₆ normal paraffins are given. The intensity parameters represent derivatives of the dipole moment with respect to variables describing vibrational distortions of individual

TABLE III
C—H Intensity Parameters in Normal Paraffins

Molecule	$\frac{\partial p_z / \partial r_{CH}}{D \text{ \AA}^{-1}}$ ^a		$\frac{\partial p_z / \partial \theta_{CH}}{D \text{ rad}^{-1}}$	
	CNDO/2	exp. ^b	CNDO/2	exp. ^b
Ethane	0.347	0.425	-0.125	-0.291
Propane	0.370	0.431	-0.114	-0.037
<i>n</i> -Butane	0.386	—	-0.099	—
<i>n</i> -Pentane	0.402	—	-0.091	—
<i>n</i> -Hexane	0.419	—	-0.086	—

^a For definition of axes and coordinates see Ref. 43, also the text.

^b From Ref. 46.

valence bonds. The set of bond coordinates used is discussed in more detail later in the text. It is seen that $\partial p_z / \partial r_{CH}$ gradients vary within narrow limits with value increasing gradually upon extending the chain in the range 0.347—0.419 D/Å. The deformation bond parameters are also fairly constant in the series of hydrocarbons studied with values decreasing from 0.125 to 0.086 D/rad. From experiment intensity data for ethane and propane are available.⁴⁶ The intensity parameters $\partial p_z / \partial r_{CH}$ and $\partial p_z / \partial \theta_{CH}$ for ethane and propane evaluated from the experimental p/S_j derivatives are also given in Table III. The experimental $\partial p_z / \partial r_{CH}$ gradients for ethane and propane are very close, in accord with the theoretical prediction. In the case of the deformation bond parameters, however, considerable difference is found, whilst the theoretical values are close. The available data do not allow to assess the origine of this discrepancy. In general, the theoretical data obtained show that C—H bond dipole derivatives associated with the symmetric stretching and deformation methyl modes are transferable in the series of molecules studied. The systematic variations in value upon extending the chain should be attributed to the changing, though insignificantly electronic structure of the C—H bonds.

In order to study the effect of polar substituents on the magnitude of the bond dipole derivatives similar calculations were performed for C₁—C₄ normal paraffins and their 1-fluoro and 1-nitro derivatives.⁴⁵ The analysis was confined to vibrations of an end methyl group. In non-substituted methane the vibrations studied refer to CH₃D isotope. C—H bond parameters associated with symmetric and asymmetric methyl vibrations derived from CNDO/2 calculations are summarized in Table IV. As mentioned the coordinates Δr_k , $\Delta \theta_k$ and $\Delta \varphi_k$ specify the changes in length and orientation of individual bonds (see the following section). The theoretical predictions show that bond parameters in CH₃D, CH₃F and CH₃NO₂ are quite different from the corresponding quantities in the other molecules studied. Thus, even in non-substituted methane, the band intensities cannot be interpreted in terms of common set of parameters with the higher homologues. As expected, the polar substituents in methane induce large changes in parameter values. Even the sign of some parameters is reversed. Much smaller changes in C—H bond parameters are caused by polar substitution in the ethane series. Some of the parameters are even transferable. The corresponding parameters in propane and

butane and their substituted derivatives are quite constant in value. Thus, two methylene groups almost entirely eliminate the influence of highly polar substituents on the electronic structure of the C—H bonds belonging to the end methyl group.

In the last column of Table IV the calculated equilibrium dipole moments for the molecules studied are given. It has been feared that polar parameters representing derivatives of the total dipole moment may depend on its magnitude. If so, such quantities cannot be considered as reflecting local properties of molecular sub-units. Results presented in Table IV, however, definitely show that such assumptions are groundless. Very significant variations in dipole moment value in the propane and butane series do not practically affect the magnitude of the bond parameters.

TABLE IV

Comparison of Bond Polar Parameters for Methyl C—H Bond in C₁—C₄ n-Paraffins and their 1-Fluoro and 1-Nitro Derivatives^a

Molecule	$\frac{\partial p_z}{\partial r_1}^b$ D Å ⁻¹	$\frac{\partial p_z}{\partial \Theta_1}$ D rad ⁻¹	$\frac{\partial p_x}{\partial r_1}$ D Å ⁻¹	$\frac{\partial p_x}{\partial \Theta_1}$ D rad ⁻¹	$\frac{\partial p_y}{\partial \varphi_1}$ D rad ⁻¹	$\frac{p_0}{D}$
CH ₃	0.184	-0.240	0.787	0.096	0.335	0
CH ₃ F	0.286	0.061	0.897	-0.282	0.057	1.66
CH ₃ NO ₂	0.053	-0.247	0.210	-0.145	0.705	4.38
C ₂ H ₆	0.345	-0.128	1.091	0.341	0.175	0
C ₂ H ₅ F	0.241	-0.252	0.851	0.426	0.401	1.83
C ₂ H ₅ NO ₂	0.213	-0.266	0.746	0.331	0.470	4.52
C ₃ H ₈	0.368	-0.116	1.189	0.331	0.144	0.002
C ₃ H ₇ F	0.345	-0.139	1.056	0.288	0.179	1.85
C ₃ H ₇ NO ₂	0.330	-0.149	0.965	0.304	0.218	4.62
C ₄ H ₁₀	0.383	-0.101	1.208	0.350	0.143	0
C ₄ H ₉ F	0.362	-0.119	1.148	0.338	0.172	1.87
C ₄ H ₉ NO ₂	0.350	-0.129	1.082	0.331	0.211	4.67

^a Calculated using CNDO/2 method and standard geometry (Ref. 29).

^b z-axis is oriented symmetrically with respect to the end methyl group and directed from the end carbon towards heteroatom or internal carbon. r₁ (CH) bond of the end methyl group lies in the x, z-plane. For coordinate definition see text.

Concluding, the MO results discussed indicate that intensity parameters in the molecules studied are determined by local charge fluctuations and reflect, in most general terms, dynamic polar properties of the valence bonds involved in the vibration. Such dipole derivatives may form an appropriate basis for parametric interpretation of infrared band intensities.

In the following sections an approach to a parametric analysis of IR intensities is described formulated on the basis of the theoretical results discussed

so far.^{11,12} The set of empirical molecular parameters satisfies the following preconditions:

(1) The parameters represent derivatives of the total dipole moment. The point-charge approach is avoided.

(2) The dipole derivatives are associated with vibrational distortions of individual valence bonds.

(3) Explicit distinction between parameters determined from band intensities of stretching and bending modes. This leads to simpler physical significance of the bond parameters.

(4) The number of parameters equals the number of experimental observables.

BOND POLAR PARAMETERS: DEFINITIONS AND EVALUATION

The vibrational motion of molecules is defined in terms of the following coordinates:

(a) Changes of bond lengths, defining as usual stretchings of the valence bonds, Δr_k , with k — a bond index.

(b) Changes of the angles that each bond in a molecule forms with the z -axis of an arbitrary space-fixed cartesian reference system, $\Delta \Theta_k$.

(c) Changes in the x, y -plane of the bond rotation angle around the z -axis, $\Delta \varphi_k$.

Thus vibrational motion of an N -atomic non-cyclic molecule having $N-1$ bonds is described by $3N-3$ coordinates, which equals the vibrational degrees of freedom plus the three rotations. Therefore, rotational contributions to intensities have to be considered in the analysis.

The intensity parameters to be determined, termed bond polar parameters, represent derivatives of the cartesian components of the total dipole moment with respect to the variables Δr_k , $\Delta \Theta_k$ and $\Delta \varphi_k$. These form the following matrices for a bond k :

$$s_k = \begin{pmatrix} \partial p_x / \partial r_k \\ \partial p_y / \partial r_k \\ \partial p_z / \partial r_k \end{pmatrix} \quad d_k = \begin{pmatrix} \partial p_x / \partial \Theta_k & \partial p_x / \partial \varphi_k \\ \partial p_y / \partial \Theta_k & \partial p_y / \partial \varphi_k \\ \partial p_z / \partial \Theta_k & \partial p_z / \partial \varphi_k \end{pmatrix} \quad (14)$$

Arranged in a row all s_k and d_k form the matrix of bond polar parameters, \mathbf{P}_b :

$$\mathbf{P}_b = (s_1 d_1 s_2 d_2 \dots s_{N-1} d_{N-1}) \quad (15)$$

The transformation of the integrated infrared intensities, A_i , into bond polar parameters involves several steps. $\partial p / \partial Q_i$ dipole gradients are obtained according to Eq. (2). The removal of the sign ambiguity for the $\partial p / \partial Q_i$ values can be achieved by analysis of the Coriolis interactions present⁴⁷, a check of the equivalence of dipole gradients of isotopic molecules, G -sum rule analysis,⁴⁸ as well as quantum mechanical calculations. It should be said that at present such data are available only for relatively small molecules of higher symmetry.

$\partial p / \partial Q_i$ are converted into dipole derivatives with respect to symmetry coordinates by the normal coordinate transformation⁴⁹

$$\frac{\partial \mathbf{p}}{\partial \mathbf{Q}} \mathbf{L}_S^{-1} = \frac{\partial \mathbf{p}}{\partial \mathbf{S}} = \mathbf{P}_S \quad (16)$$

\mathbf{L}_S is the transformation matrix between normal and symmetry coordinates. At this stage accurate knowledge of the potential force field is necessary. The determination of reliable force field is plagued by a variety of well known difficulties. It is important to point out that the transformation of band intensities to polar parameters is very sensitive to the force field employed. Again, there are reasonable chances to determine accurate force field for small and symmetrical molecules only.

Bond polar parameters are determined using the following matrix expression:

$$\mathbf{P}_b = \mathbf{P}_S \mathbf{V} \mathbf{A}_S \quad (17)$$

The matrix \mathbf{V} defines the intensity coordinates Δr_k , $\Delta \Theta_k$ and $\Delta \varphi_k$ in terms of atomic cartesian displacements¹², and \mathbf{A}_S is determined according to the known relation⁵⁰:

$$\mathbf{A}_S = \mathbf{M}^{-1} \tilde{\mathbf{B}}_S \mathbf{G}_S^{-1} \quad (18)$$

\mathbf{M} , \mathbf{B}_S and \mathbf{G}_S have their usual meaning.⁴⁹

The rotational contributions to both sides of Eq. (17) have to be eliminated and this can be achieved following the methodology of the heavy-isotope approach introduced by Van Straten and Smit.⁵¹ In cases of molecules with a non-zero permanent dipole moment the following equation is used in determining bond polar parameters:

$$\mathbf{P}_S^{\text{corr}} = \mathbf{P}_b \mathbf{V} \mathbf{A}_S^* \quad (19)$$

$\mathbf{P}_S^{\text{corr}}$ contains rotationally corrected dipole moment derivatives with respect to symmetry coordinates. By an asterisk we denote the \mathbf{A} matrix of the heavy non-rotating isotope. Both sides of Eq. (19) do not involve rotational terms and the elements of \mathbf{P}_b are easily calculated from the sets of linear equations for each symmetry species.

APPLICATION: ANALYSIS OF THE GASE-PHASE IR INTENSITIES OF METHYL HALIDES

The bond polar parameter method has been applied in interpreting gas-phase infrared intensities of several classes of molecules.⁵²⁻⁵⁴ Here we report the results from the analysis of IR intensities in the methyl halide series. Gas-phase infrared band intensities for these molecules were accurately determined in 1966 by Russell, Needham and Overend.⁵⁵ More recently the band intensities of methyl bromide, methyl fluoride and methyl chloride have been remeasured. In the present work we have used the experimental data of Russell, Needham and Overend⁵⁵ for methyl chloride and methyl iodide, the results of Kondo and Saeki for methyl fluoride⁵⁷ and of van Straten and Smit for methyl bromide⁵⁶.

The internal and intensity coordinates, and the Cartesian reference system employed are defined in Figure 1. The symmetry coordinates are those suggested by Aldous and Mills⁵⁹, shown in Table V together with the molecular geometry parameters. The preferred set of $\partial p / \partial S_j$ -values for methyl fluoride and methyl bromide have been taken from the studies of Kondo and Saeki⁵⁷ and van Straten and Smit⁵⁶, respectively. These are averaged values from two isotopes — CH_3X and CD_3X . We have recalculated the dipole moment derivatives with respect to symmetry coordinates for CH_3Cl and CH_3I using the more recent force fields of Duncan, McKean and Speirs⁶⁰. The calculated \mathbf{L}_S

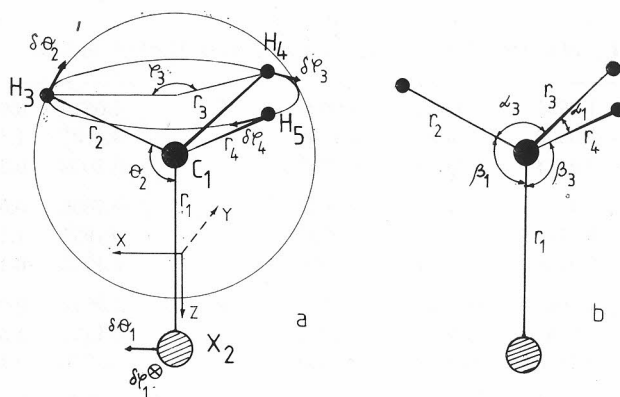


Figure 1. Definitions of intensity coordinates and Cartesian reference system (a) and of internal coordinates (b) for methyl halides. Bond directions are from atom with smaller number to atom with greater number.

TABLE V
Geometry Parameters and Symmetry Coordinates for Methyl Halides

	r_{CX} Å	r_{CH} Å	α_{CH} deg.
CH ₃ F	1.095	1.382	110°30'
CH ₃ Cl	1.084	1.778	110°50'
CH ₃ Br	1.084	1.935	111°20'
CH ₃ I	1.083	2.136	111°40'

Symmetry coordinates^b:

$$S_1 = 3^{-1/2} (\sum^4 \Delta r_i)$$

$$A_1 \quad S_2 = (k \sum^{i=2} \Delta \alpha_i - \sum \Delta \beta_i) / [3(1+k^2)]^{1/2}, \quad k = -3 \sin \beta \cos \beta / \sin \alpha$$

$$S_3 = \Delta r_1$$

$$S_{4a} = 6^{-1/2} (2 \Delta r_2 - \Delta r_3 - \Delta r_4) \quad S_{4b} = 2^{-1/2} (\Delta r_3 - \Delta r_4)$$

$$E \quad S_{5a} = 6^{-1/2} (2 \Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3) \quad S_{5b} = 2^{-1/2} (\Delta \alpha_2 - \Delta \alpha_3)$$

$$S_{6a} = 6^{-1/2} (2 \Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3) \quad S_{6b} = 2^{-1/2} (\Delta \beta_2 - \Delta \beta_3)$$

^a as given in Ref. 60.

^b from Ref. 59.

matrices for methyl chloride, methyl iodide and their fully deuterated isotopes are given in Table VI. The $\partial p / \partial S_j$ -quantities forming the \mathbf{P}_S polar tensor are also H₃/D₃-isotopically averaged.

The sign choice for A₁ and E symmetry classes for CH₃F is (+ — —, — + +), resulting from experimental⁵⁷ and *ab initio* quantum mechanical⁶¹ data. The

TABLE VI
 L_S Matrices for Methyl Chloride and Methyl Iodide^a

CH ₃ Cl	A ₁	1.0081	0.0011	-0.0039	E	1.0510	0.0209	-0.0013
		-0.0939	1.3897	0.1668		0.1131	1.5134	-0.2284
		-0.0433	0.0840	0.3202		-0.1012	0.3207	0.9136
CD ₃ Cl	A ₁	0.7215	0.0116	0.0022	E	0.7806	0.0005	0.0072
		-0.1475	1.0710	0.0198		0.1937	1.1108	-0.1022
		-0.0654	0.1484	0.2918		-0.1213	0.1564	0.6817
CH ₃ I	A ₁	1.0065	-0.0286	-0.0027	E	1.0514	0.0191	-0.0172
		-0.0481	1.3722	0.1307		0.1171	1.5359	-0.1592
		-0.0388	0.0970	0.2832		-0.0740	0.2729	0.9149
CD ₃ I	A ₁	0.7198	-0.0136	0.0022	E	0.7813	0.0006	-0.0062
		-0.1024	1.0572	0.0397		0.1971	1.1234	-0.0682
		-0.0571	0.1475	0.2571		-0.1077	0.1249	0.6835

^a Calculated from the force fields determined by Duncan, McKean and Speirs (Ref. 60). Units are amu^{-1/2} or rad amu^{-1/2} Å⁻¹ depending on whether S_j are in Å or in rad.

sign combination (+ — —, — + —) was adopted for the three other molecules of the series being also in accord with *ab initio* and CNDO MO calculations for methyl chloride and methyl bromide, respectively.^{56,61} The observed Coriolis intensity perturbations between infrared bands in CD₃Cl are also in agreement with this sign combination⁵⁸.

Finally, the elements of the \mathbf{P}_S matrices, resulting from the preferred sign combinations for the $\partial p/\partial Q_i$ derivatives, are as follows:

CH₃F

$$\mathbf{P}_S = \begin{pmatrix} S_1 & S_2 & S_3 & S_{4a} & S_{5a} & S_{6a} & S_{4b} & S_{5b} & S_{6b} \\ 0 & 0 & 0 & -0.72 & 0.29 & 0.02 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -0.72 & 0.29 & 0.02 \\ 0.64 & 0.20 & -4.54 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} p_x \\ p_y \\ p_z \end{matrix}$$

CH₃Cl

$$\mathbf{P}_S = \begin{pmatrix} 0 & 0 & 0 & -0.40 & 0.144 & -0.415 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -0.40 & 0.144 & -0.415 \\ 0.60 & -0.174 & -2.15 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} p_x \\ p_y \\ p_z \end{matrix}$$

CH₃Br

$$\mathbf{P}_S = \begin{pmatrix} 0 & 0 & 0 & -0.216 & 0.353 & -0.359 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -0.216 & 0.353 & -0.359 \\ 0.576 & -0.317 & -1.546 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} p_x \\ p_y \\ p_z \end{matrix}$$

CH₃I

$$\mathbf{P}_S = \begin{pmatrix} 0 & 0 & 0 & -0.136 & 0.347 & -0.380 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -0.136 & 0.347 & -0.380 \\ 0.492 & -0.454 & -0.533 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} p_x \\ p_y \\ p_z \end{matrix}$$

The dipole moment derivatives are corrected for rotational contributions using rotational corrections tabulated by van Straten and Smit⁵¹. The sign convention for the dipole moment is as follows: negative charge in positive direction of the Cartesian axes corresponds to a negative dipole.

As mentioned the elimination of rotational terms in the right-hand side of Eq. (17) is achieved via calculation according to Eq. (19). In the systems studied the carbon and halogen masses were multiplied by 1000. As an illustration of the calculations we adduce the complete \mathbf{VA}_S^* matrix for methyl fluoride (Table VII). The absence of rotational contributions can be easily seen in the cases of the asymmetric *S*-stretching modes (ν_{4a} , ν_{4b}). There are practically no changes in all angular coordinates, and therefore rotational reorientations of the bonds are not present. The matrix product \mathbf{VA}_S^* settles the relations between the rotation-free $\partial p/\partial S_j$ values and the bond polar parameters for each symmetry species. The solution of the resulting sets of linear equations gives the values of all elements of the *s* and *d* parametric matrices. These are shown in Tables VIII and IX.

Each C—X bond is characterized by a single parameter, $\partial p_z/\partial r_{CX}$. As seen from Table VIII there are considerable variations of the bond polar parameters associated with the stretching of the carbon-halogen bonds. Taking into account the differences in the properties of the halogen atoms transferability of this particular bond polar parameter is not expected. Its systematic variation as X changes from F to I shows, however, that the parameters could be related to the C—X bond properties. Figure 2 gives the plot of the $\partial p_z/\partial r_{CX}$ magnitudes against Pauling electronegativity values for the halogen atoms. The satisfactory correlation indicates that these parameters could characterize the polar properties of the respective bonds. It should be noted that a number of good correlations between atomic polar tensor values for methyl halides and halogen electronegativities have been found by Newton and Person⁶².

C—H stretching and deformation bond polar parameters are also not transferable in most cases, as seen from the data presented in Tables VIII and IX, although the expectations are for similarity in the electronic structure of CH₃

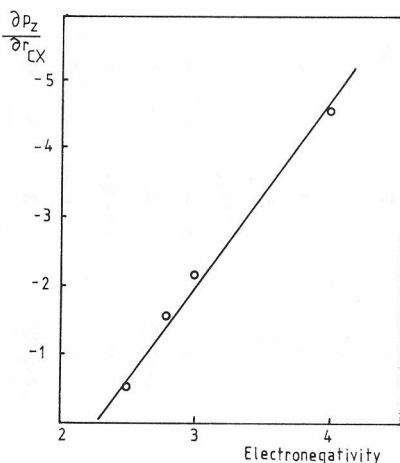


Figure 2. Plot of s_{CX} bond polar parameters versus electronegativities of the halogen atoms.

TABLE VII
VA_S Matrix for Methyl Fluoride^a*

	S_1	S_2	S_3	S_{4a}	S_{5a}	S_{6a}	S_{4b}	S_{5b}	S_{6b}
Δr_1	0	0	1.0000	0	0	0	0	0	0
$\Delta \theta_1$	0	0	0	0	0	0	0	0	0
$\Delta \varphi_1$	0	0	0	0	0	0	0	0	0
Δr_2	0.5772	0	0	0.8164	0	0	0	0	0
$\Delta \theta_1$	0	-0.4164	0	0	0	0.8164	0	0	0
$\Delta \varphi_2$	0	0	0	0	0	0	0	0.5373	-0.2579
Δr_3	0.5772	0	0	-0.4082	0	0	0.7071	0	0
$\Delta \theta_2$	0	-0.4164	0	0	0	-0.4082	0	0	0.7071
$\Delta \varphi_3$	0	0	0	0	-0.4654	0.2234	0	-0.2687	0.1290
Δr_4	0.5772	0	0	-0.4082	0	0	-0.7071	0	0
$\Delta \theta_3$	0	-0.4164	0	0	0	-0.4082	0	0	-0.7071
$\Delta \varphi_4$	0	0	0	0	0.4654	-0.2234	0	-0.2687	0.1290

^a All rotational contributions are eliminated using a heavy isotope. See text.

TABLE VIII

Bond Polar Parameters from the IR Intensities of Stretching Vibrations in the Methyl Halides^a

Molecule Intensity parameter ^b	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
s_1	$\begin{pmatrix} 0 \\ 0 \\ -4.54 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ -2.15 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ -1.546 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ -0.533 \end{pmatrix}$
s_2	$\begin{pmatrix} -0.588 \\ 0 \\ 0.370 \end{pmatrix}$	$\begin{pmatrix} -0.244 \\ 0 \\ 0.346 \end{pmatrix}$	$\begin{pmatrix} -0.176 \\ 0 \\ 0.333 \end{pmatrix}$	$\begin{pmatrix} -0.118 \\ 0 \\ 0.284 \end{pmatrix}$
s_3	$\begin{pmatrix} 0.294 \\ -0.509 \\ 0.370 \end{pmatrix}$	$\begin{pmatrix} 0.122 \\ -0.211 \\ 0.346 \end{pmatrix}$	$\begin{pmatrix} 0.088 \\ -0.153 \\ 0.333 \end{pmatrix}$	$\begin{pmatrix} 0.059 \\ -0.102 \\ 0.284 \end{pmatrix}$
s_4	$\begin{pmatrix} 0.294 \\ 0.509 \\ 0.370 \end{pmatrix}$	$\begin{pmatrix} 0.122 \\ 0.211 \\ 0.346 \end{pmatrix}$	$\begin{pmatrix} \\ \\ 0.333 \end{pmatrix}$	$\begin{pmatrix} 0.059 \\ 0.102 \\ 0.284 \end{pmatrix}$

^a In units D Å⁻¹.

^b The numbering of the bonds is shown in Figure 1.

TABLE IX

Bond Polar Parameters from IR-Intensities of Deformation Vibrations in the Methyl Halides^a

Intensity parameter ^b	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
d_2	$\begin{pmatrix} 0.130 & 0 \\ 0 & 0.360 \\ -0.160 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.124 & 0 \\ 0 & 0.462 \\ 0.112 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.160 & 0 \\ 0 & 0.442 \\ 0.249 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.186 & 0 \\ 0 & 0.428 \\ 0.354 & 0 \end{pmatrix}$
d_3	$\begin{pmatrix} -0.065 & -0.312 \\ 0.113 & -0.180 \\ -0.160 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.062 & -0.400 \\ -0.108 & -0.231 \\ 0.112 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.080 & -0.383 \\ -0.139 & -0.221 \\ 0.249 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.093 & -0.370 \\ -0.379 & -0.214 \\ 0.354 & 0 \end{pmatrix}$
d_4	$\begin{pmatrix} -0.065 & 0.312 \\ -0.113 & -0.180 \\ -0.160 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.062 & 0.400 \\ 0.108 & -0.231 \\ 0.112 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.080 & 0.383 \\ 0.139 & -0.221 \\ 0.249 & 0 \end{pmatrix}$	$\begin{pmatrix} 0.093 & 0.370 \\ 0.379 & -0.214 \\ 0.354 & 0 \end{pmatrix}$

^a In units D rad⁻¹.

^b The numbering of the bonds is given in Figure 1.

groups attached to halogen atoms. The observed distinct differences for the C—H bond polar parameters reveal once again the high sensitivity of vibrational intensities to structural changes. The intramolecular polarization effects due to the different halogen atoms are well illustrated by the variations of the s_{CH} parameters. Figure 3 gives the plot of the $\partial p_{s(z)}/\partial r_{CX}$ elements of the s_2

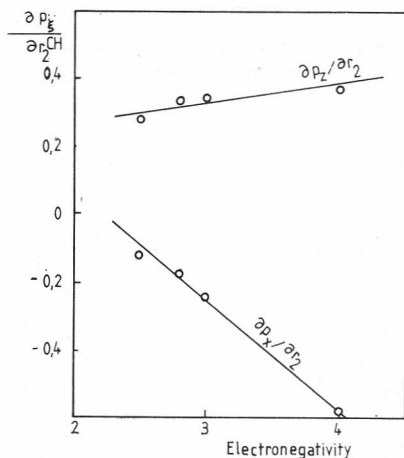


Figure 3. Plot of s_{CH} bond polar parameters *versus* halogen electronegativities in methyl halides.

vectors *vs.* halogen electronegativity values. Satisfactory correlation are obtained again. The bond parameters associated with the asymmetric C—H stretch are more sensitive to the effect of the halogen atoms.

Similar trends are also met for C—H parameters associated with the deformation modes. Notable exception from the generally identical signs of the C—H bond polar parameters are the $\frac{\partial p_x}{\partial \theta_2}$ and $\frac{\partial p_z}{\partial \theta_2}$ values of CH_3F . Considering, however, the much higher electronegativity of the fluorine atom

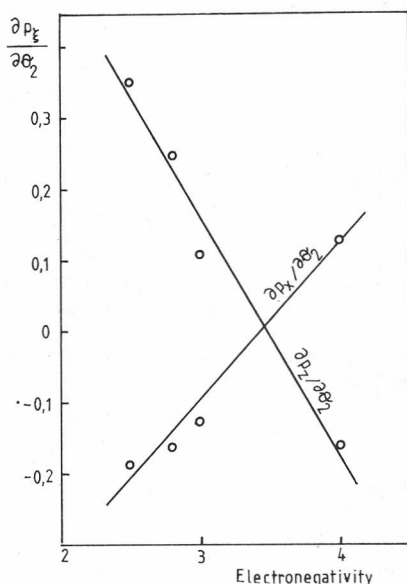


Figure 4. Plot of d_{CH} bond polar parameters against electronegativities of the halogen atoms.

and the relatively small magnitude of these parameters such changes of sign should not be regarded as surprising. This is confirmed by the plot of halogen electronegativities *versus* the parameters. Figure 4 shows the correlations between these quantities as illustrated for the case of the r_2 (CH) bond.

Comparing the results accumulated so far from applications of the bond polar parameter method, it appears that for closely related molecular systems, such as ethylene, allene, and benzene, the parameters are simply transferable⁵², while in series of molecules with significant alterations in substituents (carbonyl and thiocarbonyl halides⁵³, methyl halides) the variations in the bond polar parameters follow trends determined by intramolecular polarization effects. It may be concluded that bond polar parameters are largely determined by local structural features and could be regarded as characteristics of the dynamic polar properties of individual valence bonds.

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SAŽETAK

Intenziteti infracrvenih vrpca, raspodjela naboja u molekulama i polarna svojstva valentnih veza

Boris Galabov, Bogdana Nikolova i William J. Orville-Thomas

Razmatrana je mogućnost dobivanja raspodjele naboja u molekulama s pomoću vibracijskih intenziteta koji se eksperimentalno mogu mjeriti infracrvenom spektroskopijom. Pokazano je kako se polarni parametri veza mogu ekstrahirati iz eksperimentalnih podataka. Prodiskutirani su teorijski aspekti metode polarnih parametara valentnih veza i njezina primjena na skupinu metil-halida.