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Dipole Moment Derivatives and Infrared Intensities of SiH₄ and SiD₄

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The complete neglect of differential overlap (CNDO/2) approximate wavefunctions have been applied to select the preferred signs for the dipole moment derivatives of SiH₄ and SiD₄ in conjunction with the experimental alternatives. The apparent sign discrepancy from earlier report has been identified. The effective atomic charge for hydrogen was found to be $\chi_H/e = 0.229$, more than two times larger in comparison with the values of typical hydrocarbons like CH₄. The anomalously large effective hydrogen charge was interpreted based on a quantum mechanical model as well as the value of atom anisotropy relative to effective atomic charge.

Introduction

Of the many pioneers in molecular spectroscopy, Mulliken was possibly the first to emphasize the importance of infrared intensities[1]. He recognized that understanding this kind of data is essential for solving the central problem of chemistry; that is, for establishing the relationship between the properties of a material and its structure. However, during most of the period following Mulliken's paper, only limited progress was made in interpreting infrared intensities. Based on his paper, it was taken as self-evident that an interpretive model of intensities must be founded upon the chemical bond concept. Recent efforts to resolve dipole moment derivatives into derivatives of chemical bond moments have resulted in sets of terms in which those describing the interactions between different bonds are of the same magnitudes as those defining the properties of one particular bond[2]. Thus, unlike molecular energies, infrared intensities cannot be adequately reduced to a sum of terms that can be assigned to particular chemical bonds because of the importance of the interaction terms.

The problem of interpreting infrared intensities has improved dramatically within the last 10 years. That was because of the emergence of the concept of dipole moment derivatives as properties of the atoms in a molecule, rather than as properties of its chemical bonds. The atomic properties derived from

intensities are, then, contained in the so-called atomic polar tensors[3,4] and effective atomic charges[5]. The atomic polar tensor for atom α in a molecule is defined as the conjugate (transposed) gradient of the molecular dipole moment vector, P, written in various notations as[3]

$$P_x^\alpha = \nabla_\alpha^* P \equiv \begin{bmatrix} \partial P_x/\partial X_\alpha & \partial P_x/\partial Y_\alpha & \partial P_x/\partial Z_\alpha \\ \partial P_y/\partial X_\alpha & \partial P_y/\partial Y_\alpha & \partial P_y/\partial Z_\alpha \\ \partial P_z/\partial X_\alpha & \partial P_z/\partial Y_\alpha & \partial P_z/\partial Z_\alpha \end{bmatrix} \quad (1)$$

and the square of the effective atomic charge is defined as one-third of the sum of squares of the polar tensor components[6], that is,

$$\chi_\alpha^2 \equiv (1/3) \, \nabla_\alpha^* P : \nabla_\alpha P. \quad (2)$$

This development has led to the discovery of surprising order in intensity data. The polar tensors for a few, but ubiquitous atoms like hydrogen and fluorine, seem to be transferable properties that are characteristic of these atoms to a good approximation[7-12]. Furthermore, the analysis of the integrated intensities of a variety of hydrocarbons, fluorocarbons, and other materials with diverse structures revealed that the effective charges for the hydrogen and fluorine atoms in these systems fell within fairly narrow range of values[5,13].

Above observations encourage further testing of the atomic

polar tensor and effective charges for various hydrogen compounds. In this paper we report the interpretation of the intensities of silane, which is the extension of our works on other systems like HCN^{14}, $C_2H_2^{15}$, SF_6^{16}, CHF_3^{17}, SO_2^{18}, $CHCl_3^{19}$, $C_2N_2^{20}$, and SiF_4^{21}. Previously Prasad *et al.*[22] reported the effective hydrogen charge of SiH_4. However, their criterion for choosing the preferred signs for the dipole derivatives with respect to normal coordinates that the correct signs correspond to values of the atomic effective charges which show a maximum difference for the central and terminal atoms was criticized not to be valid in general by many investigators[10,23]. Furthermore, according to prasad *et al.*,[22] the effective hydrogen charge seems to be considerably larger in SiH_4 than those of usual hydrocarbons. Earlier, two exceptions were noted in the interpretation of intensities as atomic properties. The effective charges observed for the hydrogen atoms in C_2H_2 and HCN were found to be about 2 times larger than the values common to the other carbon–hydrogen systems[14,15]. In the previous report, however, those anomalously large effective charges could be adequately explained by virtue of their rather ionically bonded protons[24]. We have, therefore, reinvestigated the polar tensor and effective charge of hydrogen atom in silane in order to determine definitely if the effective hydrogen charge in SiH_4 is really different from those of typical hydrocarbons like CH_4.

Method of Calculation

The experimental value of the integrated intensity of the k-th fundamental mode of a molecule has been defined in two ways[25,26],

$$A_k = (1/nl) \int \ln(I_0/I) d\omega \qquad (3)$$

or $\qquad \Gamma_k = (1/nl) \int \ln(I_0/I) d\ln\omega \qquad (4)$

where, to a good approximation,

$$A_k = \omega_k \Gamma_k \qquad (5)$$

In both, (nl) denotes the product of the concentration of the absorbing species and sample thickness, I_0 and I are the incident and transmitted light intensity, repectively, and ω_k is the wave number at the band center. In the harmonic oscillator linear dipole approximation, the intensity is related to molecular structure in SI units by[27];

$$A_k = (\pi N_A/3 g_k) \ (\partial \hat{P}/\partial Q_k)^2 \qquad (6)$$

In this expression g_k denotes the degeneracy of the k-th mode, $(\partial \hat{P}/\partial K_k)$ is the derivative of the dipole vector, $\hat{P}$, with respect to the normal coordinate Q_k, and the other symbols have their customary meaning.

To obtain structural information from intensities it is necessary to transform from normal coordinates to some other more interpretable coordinate set. Until recently, bond and valence angle coordinates, $R \equiv \{R_j\}$, were always chosen, and intensities were interpreted in terms of bond moments. Using the chain rule of differentiation, the transformations are readily carried out,

$$(\partial \hat{P}/\partial Q) = (\partial \hat{P}/\partial R) \ (\partial R/\partial Q) \qquad (7)$$

and $\qquad (\partial \hat{P}/\partial R) = (\partial \hat{P}/\partial Q) \ (\partial Q/\partial R) \qquad (8)$

These are equivalent to expressions in the more customarily used matrix notation introduced by Person[3] and Wilson[27],

$$P_Q = P_R L \quad \text{and} \quad P_R = P_Q L^{-1} \qquad (9)$$

In (9), for example, $(P_R)_{ij} \equiv (\partial P_i/\partial R_j)$ and $(L)_{kj} \equiv (\partial R_k/\partial Q_j)$. In 1961, however, Biarge, Herranz and Morcillo[4] broke with tradition and chose, instead, an atom-centered, Cartesian coordinate system, X,

$$(\partial \hat{P}/\partial Q) = (\partial \hat{P}/\partial X)(\partial X/\partial Q) \qquad (10)$$

$$(\partial \hat{P}/\partial X) = (\partial \hat{P}/\partial Q)(\partial Q/\partial X) + (\partial \hat{P}/\partial \tau)(\partial \tau/\partial X) \qquad (11)$$

where τ denotes the set of coordinates describing rigid–body translation and rotation which must be included for completeness. Equation (10) can also be written in a matrix form like (9) as follows,

$$P_x = P_Q L^{-1} B + P_\tau \beta \qquad (12)$$

where B and β are the transformation matrices from the ordinary space fixed Cartesian coordinates to the internal coordinates and the τ coordinates in equation (11), respectively. The explicit implication of P_x is given above in equation (1), and equation (12) is, therefore, the master equation used in this work such that the so–called polar tensor P_x would be obtained from the experimental data by transforming from P_Q to P_x.

We note that we may also transform from P_x to P_Q by using the inverse relation of equation (10) to obtain,

$$P_Q = P_x A L, \qquad (13)$$

where the matrix A is the inverse transformation from internal coordinates to Cartesian coordinates, defined so that $BA = I$, a square identity matrix. Equation (13) has particular interest in that it is especially easy to calculate the polar tensor P_x from quantum mechanical procedures. One simply calculates the dipole moment at equilibrium and again after a small displacement in the well defined space-fixed X direction of the α atom. The difference in the X component divided by the displacement is taken to be the approximately the derivative,

$$\partial P_x/\partial X_\alpha \approx \Delta P_x/\Delta X_\alpha. \qquad (14)$$

The change in the total dipole moment vector when the α atom is displaced in the X direction also gives $\partial P_y/\partial X_\alpha$ and $\partial P_z/\partial X_\alpha$. Similarly we can evaluate the other terms in the polar
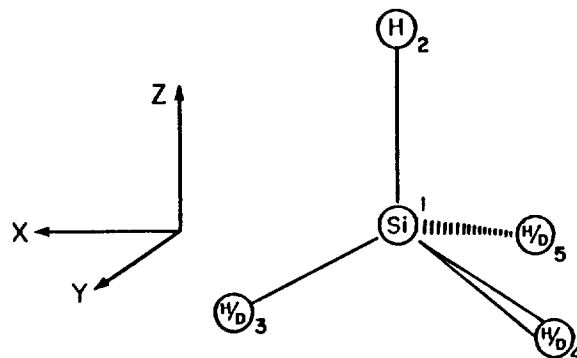

Figure 1. Coordinate axes and molecular orientation of silane used in normal coordinate calculation.

TABLE 1: Structural Data and Definition of Internal and Symmetry Coorrdinates of Silane

Masses $(u)^a$: $m_{Si} = 27.976928$ $m_H = 1.007825$ $m_D = 2.014102$

Structure^b : $R_{SiH} \doteq 0.1481\,nm$

Internal coordinates^c :

$R_1 = \delta r_{12}$	$R_6 = \delta \alpha_{214}$
$R_2 = \delta r_{13}$	$R_7 = \delta \alpha_{215}$
$R_3 = \delta r_{14}$	$R_8 = \delta \alpha_{415}$
$R_4 = \delta r_{15}$	$R_9 = \delta \alpha_{314}$
$R_5 = \delta \alpha_{213}$	$R_{10} = \delta \alpha_{315}$

Symmetry coordinates:

C_{3v} T_d

A_1 $\left\{ \begin{array}{l} A_1 \quad S_1 = (1/2)\,(R_1 + R_2 + R_3 + R_4) \\ F_x \left\{ \begin{array}{l} S_2 = (1/\sqrt{12})\,(3R_1 - R_2 - R_3 - R_4) \\ S_3 = (1/\sqrt{6})\,(R_5 + R_6 + R_7 - R_8 - R_9 - R_{10}) \end{array} \right. \end{array} \right.$

$E_x \left\{ \begin{array}{l} E_x \quad S_4 = (1/\sqrt{12})\,(2R_5 - R_6 - R_7 + 2R_8 - R_9 - R_{10}) \\ F_x \left\{ \begin{array}{l} S_5 = (1/\sqrt{6})\,(2R_2 - R_3 - R_4) \\ S_6 = (1/\sqrt{12})\,(2R_5 - R_6 - R_7 - 2R_8 + R_9 + R_{10}) \end{array} \right. \end{array} \right.$

$E_y \left\{ \begin{array}{l} E_y \quad S_7 = (1/2)\,(R_6 - R_7 - R_9 + R_{10}) \\ F_y \left\{ \begin{array}{l} S_8 = (1/\sqrt{2})\,(R_3 - R_4) \\ S_9 = (1/2)\,(R_6 - R_7 + R_9 - R_{10}) \end{array} \right. \end{array} \right.$

A_1 A_1 $S_{red} = (1/\sqrt{6})\,(R_5 + R_6 + R_7 + R_8 + R_9 + R_{10})$

^{a}Ref. (38); ^{b}Ref.(39); ^{c}The subscripts refer to the atoms shown in Figure 1; r_{ij} is a $Si_i - H_j$ bond and α_{ijk} is a $H_iSi_jH_k$ angle.

tensor P_x^z, and combine them to obtain P_x. Using equation (13), we can then convert the calculated polar tensor to P_Q, which can be compared with the experimental value.

The polar tensor values of silane were calculated by means of equation (12) using P_Q values of Ball *et al*[28]. The rotational and translational contribution to P_x, $P_x\beta$, is zero because of the null equilibrium dipole moment and charge. The Cartesian coordinate axes, numbering of atoms, and orientation of silane molecule are shown in Figure 1. The equilibrium structural data, and the definition of the internal and symmetry coordinates are listed in Table 1. The L matrices were calculated using the harmonic force field reported by Duncan[29]. These values are given in Table 2. The B matrix was evaluated using Wilson's method[27].

Results and Discussion

G sum rule graphs employing abscissas and ordinates expressed in terms of squares of atomic effective charges are very useful in comparing the accuracies of infrared fundamental sum values for isotopically related molecules. The G sum rule for silane and its deuterated analogues is given by[30]

$$[1/K]\,\Sigma\,A_i = \chi_{Si}^2\,/m_{Si} + [n_H/m_H + (4 - n_H)/m_D]\,\chi_H^2 \quad (15)$$

where $K = N_A/4\varepsilon_o\,c^2$ and ΣA_i is the fundamental intensity sum. χ_a and m_a are atomic effective charges and masses and n_H is equal to the number of hydrogens in the molecule under study. In Figure 2, graphical representations of the G sum rule for the intensity data of SiH$_4$, SiHD$_3$, and SiD$_4$ are presented. Since the ν_5 band intensity of SiHD$_3$ was not reported in Ball's paper, it has been assumed here that his value is about 30% greater than that of Levin *et al*[31]., for Ball's intensity data are 30% greater at a moderate estimate than those of Levin *et al.* for other bands in SiHD$_3$. The figure clearly shows that although the SiH$_4$, SiD$_4$, and SiHD$_3$ data of Ball *et al.* result in an in-

TABLE 2: Harmonic Force Field, Normal Coordinates, and Integrated Intensities of Silane

Harmonic force constants $(Nm^{-1})^a$:

A_1	$K_{11} = 304.8$	F	$K_{33} = 285.7$	
E	$K_{22} = 42.7$		$K_{34} = -9.6$	
			$K_{44} = 52.0$	

Normal Coordinates $(u^{-1/2})^b$:

SiH$_4$	F_x^c		Q_3	Q_4	
		S_2	1.0184	0.0534	
		S_3	-0.1150	0.9892	

SiD$_4$	F_x^c		Q_3	Q_4	
		S_2	0.7361	0.0480	
		S_3	-0.1345	0.7222	

SiHD$_3$	A_1		Q_1	Q_2	Q_3
		S_1	0.4925	0.6147	-0.0056
		S_2	0.8858	-0.3602	0.0391
		S_3	-0.0770	0.0683	0.7274
	E_x^d		Q_4	Q_5	Q_6
		S_4	-0.0211	0.7282	-0.5638
		S_5	0.7352	0.0487	0.0354
		S_6	-0.1551	0.6373	0.5282

Intensities $(Km \cdot mole^{-1})$:

		Ball & Mckean^e	Levin & King^f
SiH$_4$	$A_3(\nu_3)$	303.7 ± 3.1	320.5 ± 9.0
	$A_4(\nu_4)$	399.8 ± 4.0	296.3 ± 21.7
SiD$_4$	$A_3(\nu_3)$	176.6 ± 1.8	127.1 ± 3.4
	$A_4(\nu_4)$	210.2 ± 2.1	136.5 ± 8.3
SiHD$_3$	$A_1(\nu_1)$	96.0 ± 0.9	65.7 ± 1.3
	$A_2(\nu_2) + A_4(\nu_4)$	132.6 ± 1.3	122.1 ± 2.4
	$A_3(\nu_3) + A_6(\nu_6)$	135.9 ± 1.4	96.4 ± 9.6
	$A_5(\nu_5)$	—	80.5 ± 2.0

^{a}Ref (29); ^{b}The indices labelling the normal coordinates correspond to the labels identifying the vibrational mode given in footnote(g) below; ^{c}The K and L elements for the F_x and F_y blocks are identical with those of F_z block; ^{d}The L elements for the E_y block are identical with those of E_x block. E_x in C_{3v} point group corresponds to the combination of E_x and F_x in T_d point group. See the definition of symmetry coordinates in Table 1; ^{e}Ref (28); ^{f}Ref (31); ^{g}The indices labelling the vibrational modes correspond to the notations in ref (42).

tersection yielding positive values for χ_{Si}^2 and the isotopically invariant quantities, χ_H^2 and χ_D^2, the intersection of the G sum rule lines for the data of Levin *et al.* implies imaginary values for the effective charge of silicon atom. One must conclude that the intensity sums for the data of Levin *et al.* are less accurate and somewhat inconsistent with the sums for the data of Ball *et al.* In this respect we have employed Ball's intensity data for the subsequent analysis.

Prasad *et al*[32]. reported the preferred sign of dipole moment derivatives with respect to normal coordinates, $\partial P/\partial Q_3$ and $\partial P/\partial Q_4$, for SiH$_4$. However, as mentioned above recalculations are necessary in order to ensure that the sign conventions are consistent throughout the treatment. In Table 3 representative values for silicon atom, hydrogen atom 1, and hydrogen atom 2 of Figure 1 for the atomic polar tensors of SiH$_4$ and SiD$_4$ are given. The experimental errors for the individual polar tensor elements are given in parenthesis. The best agreement for the expected isotopically invariant elements of these ten-
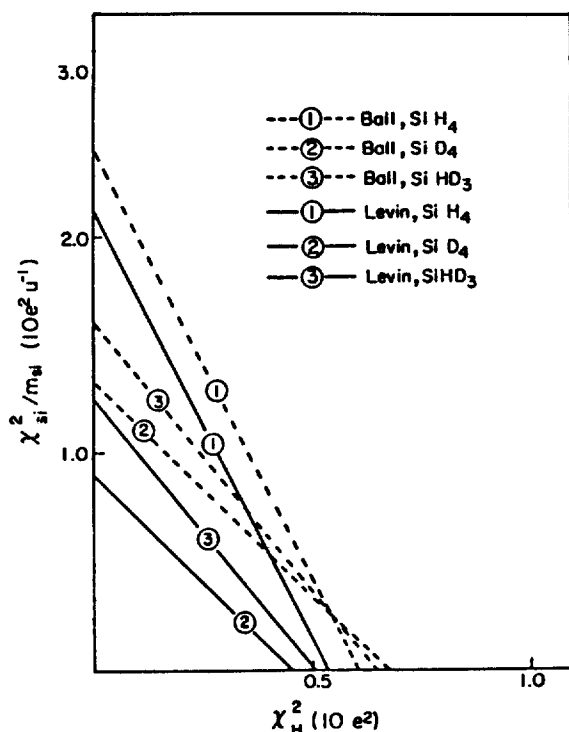
Figure 2. G-sum rule graphs for SiH_4, SiD_4, and $SiHD_3$. ----; Ball et al's data in ref. (28); ——; Levin et al's data in ref. (31).

sors occurs for the (⁻⁺) sets for SiH_4 and the (⁻⁺) sets for SiD_4. The differences between the respective polar tensor elements of these sets are either smaller than the sum of the experimental errors of these elements for SiH_4 and SiD_4 or they are slightly larger. The error estimates reported here are minimum values as they contain no contributions due to errors in the normal coordinates. Consideration of these errors could easily increase our error estimates for each of the polar tensor elements by 0.002 e which is sufficient to obtain agreement between all the individual elements of these sets.

In order to reach some decision about which of the several possible polar tensors are correct for silane, we may compare the different possible sets of the P_x values from the experimental data with the calculated values from the CNDO/2 quantum mechanical calculations, which are given in Table 4. Comparison of the calculated results with the possible experimental results leads us to prefer one sign combination. The calculated values of $\partial P/\partial S_j$ agree reasonably well in magnitude and sign with the experimental dipole moment derivatives from the (− +) sign combinations ($\partial P/\partial Q_3$ negative and $\partial P/\partial Q_4$ positive) for both of SiH_4 and SiD_4. It is generally difficult however to predict quantitatively the dipole moment derivatives from approximate quantum mechanical treatments. Nevertheless, the $\partial P/\partial S_j$ values are large enough leaving no room for doubt about the proper sign choice. In particular any doubts remaining about

TABLE 3: Atomic Polar Tensors of Silane Given in Multiples of e

		P_x^{Si}	$P_x^{H/D(2)c}$	$P_x^{H/D(3)}$
SiH_4[a]	$(\pm\,\pm)$[b]	$\begin{pmatrix} \pm0.141^{d}\,(0.005) & 0 & 0 \\ 0 & \pm0.141\,(0.005) & 0 \\ 0 & 0 & \pm0.141\,(0.005) \end{pmatrix}$	$\begin{pmatrix} \mp0.207\,(0.001) & 0 & 0 \\ 0 & \mp0.207\,(0.001) & 0 \\ 0 & 0 & \pm0.309\,(0.002) \end{pmatrix}$	$\begin{pmatrix} \pm0.251\,(0.001) & 0 & \mp0.162\,(0.001) \\ 0 & \mp0.207\,(0.001) & 0 \\ \mp0.162\,(0.001) & 0 & \mp0.150\,(0.001) \end{pmatrix}$
	$(\pm\,\mp)$	$\begin{pmatrix} \mp0.920\,(0.005) & 0 & 0 \\ 0 & \mp0.920\,(0.005) & 0 \\ 0 & 0 & \mp0.920\,(0.005) \end{pmatrix}$	$\begin{pmatrix} \pm0.227\,(0.001) & 0 & 0 \\ 0 & \pm0.227\,(0.001) & 0 \\ 0 & 0 & \pm0.236\,(0.002) \end{pmatrix}$	$\begin{pmatrix} \pm0.235\,(0.001) & 0 & \mp0.003\,(0.001) \\ 0 & \pm0.227\,(0.001) & 0 \\ \mp0.003\,(0.001) & 0 & \pm0.228\,(0.001) \end{pmatrix}$
SiD_4[a]	$(\pm\,\pm)$	$\begin{pmatrix} \pm0.080\,(0.005) & 0 & 0 \\ 0 & \pm0.080\,(0.005) & 0 \\ 0 & 0 & \pm0.080\,(0.005) \end{pmatrix}$	$\begin{pmatrix} \mp0.202\,(0.001) & 0 & 0 \\ 0 & \mp0.202\,(0.001) & 0 \\ 0 & 0 & \pm0.344\,(0.002) \end{pmatrix}$	$\begin{pmatrix} \pm0.283\,(0.002) & 0 & \mp0.171\,(0.001) \\ 0 & \mp0.202\,(0.001) & 0 \\ \mp0.171\,(0.001) & 0 & \mp0.141\,(0.001) \end{pmatrix}$
	$(\pm\,\mp)$	$\begin{pmatrix} \mp0.910\,(0.005) & 0 & 0 \\ 0 & \mp0.910\,(0.005) & 0 \\ 0 & 0 & \mp0.910\,(0.005) \end{pmatrix}$	$\begin{pmatrix} \pm0.227\,(0.001) & 0 & 0 \\ 0 & \pm0.227\,(0.001) & 0 \\ 0 & 0 & \pm0.228\,(0.002) \end{pmatrix}$	$\begin{pmatrix} \pm0.238\,(0.002) & 0 & \mp0.000\,(0.001) \\ 0 & \pm0.227\,(0.001) & 0 \\ \mp0.000\,(0.001) & 0 & \pm0.227\,(0.001) \end{pmatrix}$
SiH_4	CNDO/2[e]	$\begin{pmatrix} 1.178 & 0 & 0 \\ 0 & 1.178 & 0 \\ 0 & 0 & 1.178 \end{pmatrix}$	$\begin{pmatrix} -0.311 & 0 & 0 \\ 0 & -0.311 & 0 \\ 0 & 0 & -0.261 \end{pmatrix}$	$\begin{pmatrix} -0.267 & 0 & -0.016 \\ 0 & -0.311 & 0 \\ -0.016 & 0 & -0.305 \end{pmatrix}$

[a]Intensities of silane in ref. (28) were used in this calculation; [b]The signs are the signs of the $\partial P/\partial Q_j$'s. For example, $(\pm\,\pm)$ would mean that the signs of $\partial P/\partial Q_3$ and $\partial P/\partial Q_4$ are both either positive or negative; [c]The atomic polar tensor of hydrogen atom number 2 in Figure 1. [d]The value with upper sign (+0.141) is, for example, the tensor element obtained from the signs of $\partial P/\partial Q_j$'s corresponding to the upper sign combination (+ +) in two sets of sign choices $(\pm\,\pm)$. See note b above; The values in parenthesis represent the uncertainties based on the estimated errors in the reported intensities; [e]These tensors were calculated using the CNINDO program 141 from QCPE.

TABLE 4: Comparison of Experimental and Calculated Values of $\partial P/\partial S_j$'s for Silane in Units of e

			$\partial P_x/\partial S_{2x}$	$\partial P_x/\partial S_{3x}$
Exptl	SiH₄	$(\pm\ \pm)^n$	± 0.356	± 0.355
			(0.002)	(0.002)
		$(\pm\ \mp)$	± 0.273	∓ 0.389
			(0.002)	(0.002)
	SiD₄	$(\pm\ \pm)$	± 0.397	± 0.345
			(0.002)	(0.002)
		$(\pm\ \mp)$	± 0.263	± 0.389
			(0.002)	(0.002)
Calcd	CNDO/2		-0.302	$+0.532$

ᵃSee the notes in Table 3.

TABLE 5: Effective Hydrogen Charges for Various Compounds in Natural Units(e)

SiH₄	0.229[a]	C₃H₈	0.105[i]
HCN	0.231[b]	CH₃F	0.095[j]
C₂H₂	0.198[c]	CH₃Cl	0.068[k]
CH₄	0.096[d]	CH₃Br	0.068[l]
C₂H₆	0.106[e]	CH₃I	0.071[m]
C₂H₄	0.093[f]	CH₂F₂	0.115[n]
C₆H₆	0.096[h]	CHF₃	0.048[o]

[a]This work; [b]Ref (14); [c]Ref (15); [d]Ref (10); [e]Ref (40); [f]Ref (3); [h]Ref (41); [i]Ref (40); [j]Ref (32); [k]Ref (32); [l]Ref (32); [m]Ref (32); [n]Ref (9); [o]Ref (17).

the certainty of the $(-\ +)$ sign choice may be dispelled by careful examination of Table 3, comparing the atomic polar tensors calculated by the quantum mechanical method with those obtained from the experimental data. Although there may still be some doubt on the possibility of signs of $\partial P/\partial Q_3$ and $\partial P/\partial Q_4$ being both positive, this sign choice gives the polar tensors not only considerably small in magnitude for silicon atom but also exact opposite in sign for the P_{zz} element of $P_T^{H(2)}$. It is therefore quite clear that the values calculated agree with the $(-\ +)$ sign choice and do not agree with the values derived from other sign choices. Thus we believe that the examination of intensity data in the form of atomic polar tensors may be useful in trying to decide such delicate matters as the sign choice to be preferred.

As described above prasad *et al*[22]. suggested that one criterion for choosing the preferred signs for the $\partial P/\partial Q_i$'s be that the signs should be preferred that resulted in a maximum value for the difference between the square of the effective charge χ^2_{Si} on the central atom (here silicon) and the sum of χ^2_H values for the terminal atoms (here hydrogen)[6]. The preferred sign choices for SiH₄ and SiD₄ give $\chi^2_{Si}-4\chi^2_{H/D}$ be 0.635 and 0.621 e^2, respectively which correspond to the maximum differences found by prasad *et al*. However, since we do not believe there is any physical reason to prefer a maximum or minimum value for this function, we suggest that this criterion be abandoned. Incidently, it is of some interest to note that prasad *et al*[22] obtained the different sign choice $(-\ -)$ using their criterion although their values of effective charges were almost the same as we got. However, one must realize that the signs of $\partial P/\partial Q_i$ values are meaningless without the detailed knowledge of all the definitions used to obtain them. Comparing prasad *et al*.'s values of χ^2_a with ours shows that their $(-\ -)$ convention for the signs of $\partial P/\partial Q_i$'s corresponds to our $(-\ +)$ convention. We believe there was an inconsistency in the definitions of their normal coordinate calculation.

The results reported here provides additional information on the nature of hydrogen atom effective charges. Since both elements of carbon and silicon belong to group IV in periodic table, it may be interesting to compare the effective hydrogen charge of silane with those of various hydrocarbons. Table 5 contains the effective charges of hydrogen atom for various compounds. This table reveals rather surprising feature that the effective hydrogen charges fall within the ranges

$$\chi_H = 0.12 \pm 0.11 e$$

in all of the systems listed in Table 5. These results suggest that the effective charge represents a particularly localized combination of chemical bond properties[2], whose magnitude is most sensitive to the nature of the particular atom and much less sensitive to the nature of other atoms in its vicinity or their geometrical arrangement. It is curious, however, that the effective hydrogen charge in silane shows significant difference from the "typical" value of about 0.1 e for all compounds in Table 5 except C₂H₂ and HCN. The anomalously large effective hydrogen charges in C₂H₂, HCN, and SiH₄ ,must be rationalized. Just as there is no obvious reason that the effective hydrogen charge in some compounds should be equal, there is no obvious reason that the effective charge for other compounds should deviate so sharply from the others. Indeed, it may not be clear which are the anomalous systems. Whichever point of view is chosen, one cannot resist pointing out one major difference between the properties of hydrogen atoms considered in Table 5. On the basis of author's recent finding[24] that the value of the atom anisotropy relative to the effective atomic charge is a very useful parameter in characterizing chemical bonds in terms of atomic properties, C₂H₂, HCN and SiH₄ fall into one group and other compounds in Table 5 fall into another group. The atom anisotropy, β^2, has been defined as[32]

$$\chi^2_a = (\bar{P}_a)^2 + (2/9)\ \beta^2_a \tag{16}$$

where χ_a is the effective charge of atom a in a molecule and $\bar{P}_a$ is the so-called mean dipole derivative defined as[32]

$$\bar{P}_a = \frac{1}{3}\ Tr\ P_x^a \tag{17}$$

that is, one third of the trace of atomic polar tensor of atom a. The values of author's new parameter[24], a_H $(\equiv |\frac{\sqrt{2}\beta_H}{3\chi_H}|)$ for C₂H₂, HCN and SiH₄ are close to 0, the value for a fixed charge. On the other hand, the values of a_H for other molecules in Table 5 are rather close to 1. The differences in the values of a_H between these two groups of molecules may indicate the different extent of the mobility of the hydrogen atoms in the molecular systems considered here. According to the argument given in the previous report[24] for the cases of HCN and C₂H₂, the anomalously large effective hydrogen charge in SiH₄ may be ascribed to the largely ionic character of its bonded protons

in comparison with typical hydrocarbons like CH_4. Indeed, semi-empirical CNDO/2 calculation has shown in this work that Mulliken's net hydrogen charge[35,36] in SiH_4 is more than 10 times greater compared with that of CH_4. These observations would, perhaps, be indicative of the fact that the problem of interpreting infrared intensities can be treated in a more simple and precise way by using the so-called "atomic effective charge".

To further understanding of the anomalously large hydrogen atom effective charge in silane compared with those of hydrocarbons, it will be useful to consider a quantum mechanical model for the polar tensor. Formal expressions for the polar tensor are readily obtained by computing the gradient of the dipole moment. The dipole moment is a measure of the vector difference between the centroids of positive and negative charges in a molecule. For example, in the Born–Oppenheimer approximation this difference is defined, in natural unit[33], as

$$\hat{P}(\hat{R}) = \Sigma_\eta \hat{R}_\eta q_\eta - \int \hat{r}_\rho (\hat{r} \; ; \; \hat{R}) d^3\hat{r} \qquad (18)$$

in which $\hat{R}$ denotes the set of nuclear position vectors, $\hat{R}_\eta$, q_η the atomic number of nucleus η, and

$$\rho (\hat{r} \; ; \; \hat{R}) = \int | \psi(\hat{r}, \hat{r}_2, \cdots, \hat{r}_N|^2 d^3\hat{r}_2 \cdots d^3\hat{r}_N \qquad (19)$$

the electron number density at point $\hat{r}$ in an N–electron molecule. Any model dependence in a calculation of polar tensor is introduced by way of the representation chosen for the number density function, $\rho(\hat{r};\hat{R})$ or equivalently, the molecular wave function, $\psi(\hat{r};\hat{R})$, in (19). Since polar tensors are expressed in terms of the Cartesian coordinates of the atoms in a molecule, $\rho(\hat{r};\hat{R})$ is most conveniently represented as a multi–centered expansion in complete sets of orthonormal atomic orbitals centered on each nucleus; that is[34],

$$\rho (\hat{r} \; ; \; \hat{R}) = \Sigma_{\alpha\beta}\Sigma_{ij} C_{\alpha\beta}^{ij} \psi_i^* (\hat{r}_\alpha) \psi_j (\hat{r}_\beta) \qquad (20)$$

in which, for example, $\hat{r}_\alpha = (\hat{r} - \hat{R}_\alpha)$, $\psi_i(\hat{r}_\alpha)$ denotes the i-th orbital centerd on nucleus α, and $C_{\alpha\beta}^{ij}$ is the the one–electron density matrix element. To further partition (20) into independent atomic contributions, the cross–terms are eliminated by expanding the orbitals centered on one nucleus in terms of orbitals centered on another,

$$\psi_i (\hat{r}_\alpha) = \Sigma_k S_{\alpha\beta}^{ik} (R_{\alpha\beta}) \psi_k^* (\hat{r}_\beta) \qquad (21)$$

where $R_{\alpha\beta} \equiv |\hat{R}_\alpha-\hat{R}_\beta|$ is the internuclear distance and $S_{\alpha\beta}^{ik} \equiv <\psi_i(\hat{r}_\alpha)|\psi_k(\hat{r}_\beta)>$ is the overlap integral. Substitution of (21) into (20),

$$\rho (\hat{r} \; ; \; \hat{R}) = \Sigma_\beta \Sigma_{ik} N_{\beta\beta}^{ik} \psi_i^* (\hat{r}_\beta) \psi_k^* (\hat{r}_\beta) \qquad (22)$$

where

$$N_{\beta\beta}^{ik} \equiv \Sigma_\alpha\Sigma_j C_{\beta\alpha}^{ij} S_{\alpha\beta}^{jk}$$

Integration of (22) over the position variables for an N electron system yields

$$N = \int \rho (\hat{r} \; ; \; \hat{R}) d^3r = \Sigma_\beta N_\beta (\hat{R}) \qquad (23)$$

where

$$N_\beta (\hat{R}) \equiv \Sigma_i N_{\beta\beta}^{ii} (\hat{R})$$

is the gross population density defined by Mulliken[35,36] Substituting (22) into (18), and making use of the relation $\hat{r} = \hat{r}_\beta + \hat{R}_\beta$, yields the molecular dipole moment as a sum over atomic terms,

$$\hat{P} (\hat{R}) = \Sigma_\beta \hat{R}_\beta \zeta_\beta (\hat{R}) - \Sigma_\beta \Phi_{\beta\beta} (\hat{R}) \qquad (24)$$

where

$$\zeta_\beta (\hat{R}) \equiv q_\beta - N_\beta (\hat{R}) \qquad (25)$$

is Mulliken's net atomic charge, and

$$\Phi_{\beta\beta} (\hat{R}) \equiv \Sigma_{i \ne k} < \psi_i (\hat{r}_\beta) | \hat{r}_\beta | \psi_k (\hat{r}_\beta) > N_{\beta\beta}^{ik} (\hat{R}) \qquad (26)$$

Differentiation of (24) finally yields the polar tensor,

$$\nabla_n^* \hat{P} = \zeta_n \hat{I} + \Sigma_\beta (\nabla_n \zeta_\beta) \hat{R}_\beta - \Sigma_\beta \nabla_n^* \Phi_{\beta\beta} (\hat{R}) \qquad (27)$$

Several models for interpreting infrared intensities can be identified with the terms in eq. (27). The first two terms, in particular, describe the polar tensor obtained in a classical atomic charge model[37]. The first term describes the contribution of a "net atomic-charge" which follows the motion of the nucleus perfectly, and the second term describes the "charge flux" resulting from the transfer of charge from one nucleus to another as the result of nuclear displacement. The third term is strictly a quantum mechanical term which has no classical analogue. This term arises solely from interference phenomena resulting from the superposition of wave functions. Unfortunately, there is no experimental way of resolving polar tensors into these terms, and they must be estimated by calculation.

The results of such calculations for two representative systems, CH_4 and SiH_4, are summarized in Table 6. There, theoretically estimated polar tensors for the hydrogen atoms in CH_4 and SiH_4, obtained by CNDO/2 calculations, are compared with those obtained from experimental intensities. In both calculations the CH and SiH bonds are coincident with the Z coordinate axis. For axes oriented in this way, the polar tensors are diagonal by symmetry, so that the diagonal elements are listed.

TABLE 6: Comparison fo Hydrogen Polar Tensors in SiH₄ and CH₄ Obtained by CNDO/2 Calculations and by Experiments, in Natural Units(e)

CH₄	XX(=YY)	ZZ
$\zeta_H \hat{I}$	0.012	0.012
$\Sigma \nabla_H \zeta_\beta \hat{R}_\beta$	0.046	0.093
$-\Sigma \nabla_H^* \Phi_{\beta\beta}$	-0.015	-0.218
$\nabla_H^* \hat{P}$(calc)	0.043	-0.113
$\nabla_H^* \hat{P}$(obs)ᵃ	0.064	-0.139
	χ_H(calc) = 0.074	χ_H(obs)ᵃ = 0.096

SiH₄	XX(=YY)	ZZ
$\zeta_H \hat{I}$	-0.150	-0.150
$\Sigma \nabla_H \zeta_\beta \hat{R}_\beta$	0.036	0.037
$-\Sigma \nabla_H^* \Phi_{\beta\beta}$	-0.197	-0.148
$\nabla_H^* \hat{P}$(calc)	-0.311	-0.261
$\nabla_H^* \hat{P}$(obs)ᵇ	-0.227	-0.232
	χ_H(calc) = 0.295	χ_H(obs)ᵇ = 0.229

ᵃRef (10); ᵇAverage of values derived from data in ref. (28). See Table 3.

Possibly the safest general conclusion to be drawn from these calculations is that all three of the constituent parts of the polar tensors, defined in eq. (27), are significant. Thus, none of the three groups of terms in eq. (27) can be completely neglected in these systems and presumably in others as well. In the two systems considered in Table 6, the "interference" term, $-\sum_{\beta} \nabla_{H1} \Phi_{\beta\beta}$, is a dominant one, but the other terms make comparable contributions. The "perfect following" term reflects, in part, the difference in the electronegativity between central (C or Si) and terminal (H) atoms. The excessively large value of this term in SiH_4 compared with that in CH_4 is consistent with the foregoing that SiH_4 is more ionic than typical hydrocarbons like CH_4. Coupled with this first term, the fairly large $XX(= YY)$ component of the "interference" term in SiH_4 seems to render the effective hydrogen charge of this molecule to be anomalously large. In addition, one may notice that, in SiH_4, the $XX(= YY)$ and ZZ components are nearly the same not only in magnitude but also in sign for the three groups of terms in eq. (27). These facts are, thus, accused of the finding that the value of the hydrogen anisotropy relative to the effective hydrogen charge in SiH_4 is close to 0, contrary to the cases of typical hydrocarbons like CH_4 whose values are rather close to 1. The XX component of the "interference term" may reflect specifically the more labile character of electrons in SiH_4 compared with CH_4. Thus, as we suggested in previous report[24], the magnitude of the atom anisotropy relative to the effective atomic charge would potentially be a very useful parameter in characterizing chemical bonds in terms of atomic properties only from the infrared intensity data.

In conclusion we see that G sum rule is very useful in comparing the accuracies of infrared fundamental sum values for isotopically related molecules, and that it is very easy to have apparent inconsistencies in signs due to inconsistencies in the arbitrary sign conventions occurring in the calculation of dipole moment derivatives, unless one person carries through the entire calculation from start to finish. When the sign conventions are consistent, the values of $\partial P / \partial S_j$ or of polar tensor elements calculated by the quantum mechanical method are in surprisingly good agreement with experiment. The best values for the H- and Si-atom polar tensors in silane are believed to be given in the $(- +)$ column of Table 3. The effective hydrogen charge was found to be $\chi_H/e = 0.229 \pm 0.002$, somewhat larger value compared with those of usual hydrocarbons. The large effective hydrogen charge in silane was ascribed to the largely ionic character of its bonded protons in comparison with typical hydrocarbons like CH_4. According to the quantum mechanical model, it was found that the "interference term" is excessively large in the polar tensors, leading to the more labile character of electrons in silane. Combined with above observations, it is likely that the value of the atom anisotropy relative to the effective atomic charge would potentially be a very useful parameter in understanding the chemical bonds solely from the vibrational intensity measurement.

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A Wittig Route to (Z)-13-Eicosen-10-one, the Pheromone of the Peach Fruit Moth, and Its Biological Activity Test

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(Z)-13-Eicosen-10-one, an active component of the sex pheromene of the peach fruit moth was synthesized from 4-oxo-tridecan-1-al and heptylidenetriphenylphosphonium ylide by Wittig reaction. The key intermediate, 4-oxo-tridecan-1-al, was synthesized by three different methods. The biological activity test of the synthetic pheromone as attractant for the male peach fruit moth was tested at several districts in Korea.

Introduction

(Z)-13-Eicosen-10-one, an active component of sex pheromone of the peach fruit moth, *Carposina niponensis* Walsingham, a major economic pest of apple, peach and other fruits was isolated by Tamaki[1] in 1977. Structurally, while most lepidopterous pheromones were characterized as unsaturated alcohols, acetates, or aldehydes of 12-, 14-, 16-, or 18-carbon chain length, the sex pheromone of the peach fruit moth is an exceptional unsaturated aliphatic ketone. Several syntheses of (Z)-13-eicosen-10-one have been reported[2]. In 1982, Yoshida[2a] reported the synthesis of (Z)-13-eicosen-10-one via salt-free Wittig reaction of heptylidenetriphenylphosphonium ylide and 4-oxo-tridecan-1-al(2). 4-Oxo-tridecan-1-al(2) was prepared from 1-(p-tolylsulfonyl) nonane and methyl 4,4-dimethoxy-butanoate. Recently, 4-oxo-tridecan-1-al(2) was synthesized by Hernandez[2a] by addition of n-nonyllithium to γ-butyrolactone followed by PCC oxidation of the resulting alcohol in his synthesis of (Z)-13-eicosen-10-one(1). In 1981, Naoshima[2c] reported a synthesis of (Z)-13-eicosen-10-one[1] via the Wittig olefination of 4-oxo-tridecan-1-al(2) with heptylidenetriphenylphosphonium ylide in toluene in the presence of 12-crown-4-ether. In this report, 4-oxo-tridecan-1-al(2) was prepared from diethyl 2-oxo-glutarate in five steps.

Institute of Agricultural Sciences in Suwon, Korea needed a fair amount of the pheromone of the peach fruit moth to conduct field test experiments in Korea. We therefore undertook to develop some practical mothods for the synthesis of the pheromone of the peach fruit moth.

We wish to report a practical synthesis of (Z)-13-eicosen-10-one(1) via the Wittig olefination of 4-oxo-tridecan-1-al (2) with heptylidene-triphenylphosphonium ylide. The key intermediate, 4-oxo-tridecan-1-al(2) was prepared by three different synthetic mothods. Also we wish to report the results of the biological activity test as attractant for males of the peach fruit moth.

Results and Discussion

It has been well established that the Wittig reaction when carried out between aliphatic aldehyde and aliphatic non-stabilized triphenylphosphonium ylide in salt-free, nonpolar solvent or in polar aprotic solvents such as DMF, DMSO or HMPA gives Z-alkenes stereoselectively[3]. It has been known that only aldehyde reacts with phosphonium ylide in the presence of ketone[4]. A simple retrosynthetic analysis (Scheme 1) reveals that 4-oxo-tridecan-1-al(2) is the key intermediate.

We have prepared 4-oxo-tridecan-1-al(2), the key intermediate by three different methods and synthesized the pheromone of the peach fruit moth by olefination reaction of 4-oxo-tridecan-1-al(2).

(1) Grignard Route. 4-Oxo-tridecan-1-al(2) was prepared from commercially available acrolein and decanoyl chloride (Scheme 2).

1,4-Addition of HBr to acrolein, followed by protection of the aldehyde portion with 1,3-propanediol afforded 2-(2-bromoethyl)-1,3-dioxane(3)[5]. Grignard reagent[6] from 2-(2-bromoethyl)-1,3-dioxane and Mg in THF was added to