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The polar tensors, effective charges, and infrared intensities of silane

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Symmetry conditions of a partially deuterated silane SiD_3H have been used to separate overlapped bands and to determine the correct signs of the dipole moment derivatives for SiH_4, SiD_4, and SiD_3H. These conditions were also able to predict the intensity of the $A_{3'}$ band of SiD_3H. Polar tensor isotopic invariance and the F and G sum rules also played a fundamental role in this work. Separation ratios, polar tensors, and effective charges of the silanes are reported.

INTRODUCTION

The polar tensor method[1] has proved to be a powerful tool in the interpretation of molecular infrared intensities. The atomic effective charge ξ_α defined by King[2] is easily written using this formalism[1] and the G-sum rule of Crawford[3] is conveniently expressed in terms of the ξ^2_α's^2:

$$k\sum_i A_i = \sum_\alpha \xi^2_\alpha / m_\alpha - \Omega, \tag{1}$$

where

$$\xi^2_\alpha = \mathrm{Tr}\ (\mathbf{P}^\alpha_X \mathbf{P}'^{\alpha}_X) \tag{2}$$

and

$$\mathbf{P}_X = \mathbf{P}_Q(\mathbf{L}^{-1}\ \mathbf{U}\ \mathbf{B}) + \mathbf{P}_\rho \boldsymbol{\beta}. \tag{3}$$

The polar tensor $\mathbf{P}_X$ of an N atom molecule is a matrix formed by the juxtaposition of the N atomic third order polar tensors $\mathbf{P}^\alpha_X$ ($\mathbf{P}'^{\alpha}_X$ is obtained by transposing $\mathbf{P}^\alpha_X$). The $\mathbf{P}_Q$ elements

$$(\mathbf{P}_Q)_{\sigma,i} = \partial p_\sigma / \partial Q_i,$$

$\sigma = x, y, z$ and $i = 1,2,...,3N-6$, are ratios of the differences in the components of the molecular dipole moment vector for vibrationaly distorted and equilibrium geometries to the very small variations in the normal coordinates for these geometrical distortions. Because mechanical and electric harmonicity is assumed, the integrated intensity A_i is proportional to $(\mathbf{P}'_Q \mathbf{P}_Q)_{ii}$. The matrix $(\mathbf{L}^{-1}\ \mathbf{U}\ \mathbf{B})$ may be defined by

$$\mathbf{Q} = (\mathbf{L}^{-1}\ \mathbf{U}\ \mathbf{B})\ \mathbf{X}, \tag{4}$$

where $\mathbf{Q}$ and $\mathbf{X}$ are column matrices whose elements are, respectively, the very small variations of the normal and Cartesian coordinates from molecular equilibrium. The $\mathbf{P}_\rho \boldsymbol{\beta}$ term is a rotational correction which depends upon the atomic masses m, the geometry and the equilibrium dipole moment. This correction vanishes when this moment is null. Using Tr for trace, one may write $\Omega = \mathrm{Tr}\ (\mathbf{P}_\rho \mathbf{P}'_\rho)$.

Both $\mathbf{P}^{(\alpha)}_X$ and ξ_α are isotopically invariant within the Born–Oppenheimer approximation. Moreover, both $\mathbf{P}^{(\alpha)}_X$ and ξ_α sometimes appear to be atomic quantities, transferable from one molecule to another in favorable cases,[2,4] or following some empirical transference rule.[5] Isotopic invariance, together with the graphical form of the Crawford sum rule, devised by Bruns,[6] have recently proved useful in the separation of overlapped spectral bands.[7,8].

Partially deuterated molecules have different molecular and electronic symmetries. $\mathbf{P}_Q$ elements depend on the atomic masses, reflecting the C_{3v} molecular symmetry of SiD_3H. However, this molecule does not have an equilibrium dipole moment, so that the $\mathbf{P}_S$ elements are not mass dependent and reflect electronic T_d symmetry. $\mathbf{P}_S$ and $\mathbf{P}_Q$ are related by the $\mathbf{L}$ matrix, which is obtained by diagonalizing the $\mathbf{G}\ \mathbf{F}$ product, $\mathbf{G}^{-1}$ and $\mathbf{F}$, respectively, being the kinetic energy and the force constant matrices. Both $\mathbf{G}$ and $\mathbf{F}$ are symmetrized according to the molecular symmetry group. Calculating the $\mathbf{L}$ elements and using information contained in the $\mathbf{P}_S$ matrix, whose symmetry is higher than that for $\mathbf{P}_Q$, relations among the $\mathbf{P}_Q$ elements are obtained. These relations, together with the experimental intensity values of the superimposed bands, allow the establishment of separation ratios. The resulting $\mathbf{P}_Q$ matrix for SiD_3H should reasonably satisfy the F and G sum rules for SiH_4 and SiD_4. There should also result sets of signs for the $\mathbf{P}_Q$ elements of SiH_4, SiD_4, and SiD_3H which yield a unique polar tensor $\mathbf{P}_X$ within the propagated experimental error. The choice of the signs of the $\mathbf{P}_Q$ elements was confirmed by semiempirical quantum mechanical calculations.

EXPERIMENTAL DATA

Experimental infrared data for gaseous silanes have been reported almost simultaneously by Levin and King[9] and Ball and McKean.[10] In Ref. 10, the Duncan and Mills[11] T_d point group symmetry coordinates have been used, reflecting the SiH_4 and SiD_4 molecular symmetry. As expected, assuming that the SiH_4 (or SiD_4) principal inertial axes are the Cartesian ones and using the Ref. 11 symmetry coordinates, each normal mode of vibration of SiH_4 (or SiD_4) corresponds to a vectorial sum of atomic displacements which is colinear to an axis. Thus, the $\mathbf{P}_Q$ matrix has two null elements in each column. Now, suppose that the Cartesian axes are rotated to the directions of the SiD_3H principal inertial axes. The rotated $\mathbf{P}_Q$ matrix does not present two null elements in each column. However, if this same rotation is applied to both sets of the three stretching and bending normal coordinates of the F_2 symmetry species, the $\mathbf{P}_Q$ matrix which refers to the rotated coordinates and axes is identical to the original one. This may be easily proved considering the twofold degeneration of the SiH_4 (or SiD_4) $\mathbf{P}_Q$ matrix. Moreover, the $\mathbf{G}$, $\mathbf{F}$, $\mathbf{L}$, and $\mathbf{P}_S$ matrices are also invariant for this transformation, but the polar tensor, $\mathbf{P}_X$, is

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not. The rotated F_2 coordinates, together with the A_1 and E ones, form a coordinate set which presents both T_d and C_{3v} point group symmetries, reflecting both SiH_4 (or SiD_4) and SiD_3H molecular symmetry. This set of coordinates is reported in Ref. 9.

The use of Ref. 9 symmetry coordinates and SiD_3H principal axes permits one to express the normal modes of vibration of SiH_4, SiD_4, and SiD_3H as linear combinations of the same symmetry movements, allowing comparison among the $\mathbf{P}_S$ element values for the three molecules. In addition, the above discussion shows that, for SiH_4 and SiD_4, the same $\mathbf{P}_S$ matrix may be obtained using the Ref. 11 symmetry coordinates and the SiH_4 (or SiD_4) principal inertial axes. However, in the case of SiD_3H, the use of a C_{3v} set as that in Ref. 12 is not convenient.

The bond length of the silanes was taken to be 1.478 Å.[13] Different intensity values are reported in Refs. 9 and 10 and the force constants also differ slightly. Consistency among the reported $\mathbf{L}$ matrices, frequencies, and force fields was confirmed during the course of our investigations. Both force fields yield almost the same $\mathbf{P}_X$ matrices and the one in Ref. 9 was arbitrarily chosen. Accordingly, harmonic frequencies reported in this reference were also used. On the contrary, the different sets of intensity values lead to quite different results.

The authors of Refs. 9 and 10 have checked their intensity values using the F sum rule. For SiH_4 and SiD_4, they have found an error about 20% in Ref. 9 and 2.2% in Ref. 10. Because of the $\Sigma_j \Gamma_j/\omega_j$ form, errors in bending intensities are stressed in the F sum rule, while errors in the stretching intensities are enhanced in the G sum rule, $\Sigma_j \Gamma_j \omega_j$. Thus, the application of the G sum rule graphical test[6] should also be made. While the Ref. 9 intensity sums fail to meet the test unless SiH_4 intensity sum is decreased by at least 15% or SiD_4 is increased by at least 16% or smaller changes in both sums are simultaneously made, Fig. 1 shows that the intensities of Ball and McKean[10] clearly define an isotopically invariant effective charge value about 0.415 e for H (or D). For SiD_3H, four band intensity values are reported in Ref. 9, but only three are presented in Ref. 10. Using Ball and McKean intensities, the G sum rule clearly indicates that the intensity of the band near 850 cm^{-1} may not be neglected, unless gross errors are admitted for the other intensity values.

CALCULATIONS

Using the symmetry coordinates and Cartesian axes defined in Ref. 9, the relations among the $\mathbf{P}_S$ and $\mathbf{P}_Q$ matrix elements of SiD_3H may be written

$$\begin{pmatrix} 0\,0\,0\,0\,x\,y\,0\,0\,0 \\ 0\,0\,0\,0\,0\,0\,0\,x\,y \\ 0\,x\,y\,0\,0\,0\,0\,0\,0 \end{pmatrix} = \begin{pmatrix} 0\,0\,0\,r\,s\,b/\sqrt{2}\,0\,0\,0 \\ 0\,0\,0\,0\,0\,0\,r\,s\,b/\sqrt{2} \\ p\,a\,q\,0\,0\,0\,0\,0\,0 \end{pmatrix} \times L^{-1}$$

or

$$pL_{11}^{-1} + aL_{21}^{-1} + qL_{31}^{-1} = 0,$$

$$rL_{44}^{-1} + sL_{54}^{-1} + bL_{64}^{-1}/\sqrt{2} = 0,$$

$$pL_{12}^{-1} + aL_{22}^{-1} + qL_{32}^{-1} = rL_{45}^{-1} + sL_{55}^{-1} + bL_{65}^{-1}/\sqrt{2},$$

and

$$pL_{13}^{-1} + aL_{23}^{-1} + qL_{33}^{-1} = rL_{46}^{-1} + sL_{56}^{-1} + bL_{66}^{-1}/\sqrt{2},$$

where L^{-1} element subindices 4, 5, and 6 may be simultaneously replaced by 7, 8, and 9, respectively. Solving this system of equations for p, q, r, and s and using Ref. 9 force field one obtains

$$p = 0.446\,451a - 0.003\,944b,$$

$$q = -0.016\,429a + 0.745\,739b,$$

$$r = -0.010\,038a + 0.477\,432b,$$

and

$$s = 0.845\,128a - 0.051\,991b.$$

According to Ref. 9, the spectral intensities provide values for a^2, b^2, $(p^2 + 2s^2)$ and $(q^2 + 2r^2)$. The above equations show that the differing molecular and electronic symmetries relate these intensities in a way dependent on the force field. Surely, the equations will be precisely satisfied only by exact intensities and $\mathbf{L}^{-1}$ matrix elements, but they should be useful in checking consistency among experimental data. For the Ref. 10 intensity data, the $b^2 = kA_{3'}$ value is missing and three checking calculations have been performed [Ref. 9 notation for frequency is used as intensity A subindices]. First, using $a^2 = kA_2$ and $(p^2 + 2s^2) = kA_{1,2'}$, two b values were obtained, one of which being much too large. This calculation shows that a and b must have the same sign and that

$$b = \pm 0.514\ e\,\mathrm{amu}^{-1/2}.$$

The resulting values for the sums

$$\sum_i A_i = 638.0\ \mathrm{km\ mol^{-1}}$$

and

$$\sum_i A_i w_i^{-2} = 69.74\ \mathrm{cm^3\ mol^{-1}}$$

do not satisfy both G and F sum rules: values about 481 $km\ mol^{-1}$ and 52.0 $cm^3\ mol^{-1}$, respectively, should have been found for consistency with the Ref. 10 intensity data of SiH_4 and SiD_4 molecules. The G sum rule expected value has been obtained by adjusting a SiD_3H line with the correct inclination through the intersection of the SiH_4 and SiD_4 lines in Fig. 1, while the F sum rule value corresponds to the mean of the $\Sigma_i A_i w_i^{-2}$ values for SiH_4 and SiD_4 reported in Ref. 10.

A second calculation was performed using $a^2 = kA_2$ and $(q^2 + 2r^2) = kA_{3,4}$. For the positive a value, $b = 0.382$ or $b = -0.368\ e\,\mathrm{amu}^{-1/2}$. Because the 3.8% difference between the absolute values of b are within experimental error, it may be written that, for both positive and negative a values

$$b = \pm 0.375\ e\,\mathrm{amu}^{-1/2}.$$

Then,

$$\sum_i A_i = 517.0\ \mathrm{km\ mol^{-1}}$$

and

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$$\sum_i A_i w_i^{-2} = 53.64 \text{ cm}^3 \text{ mol}^{-1},$$

which differ by only 7.5% and 3.2%, respectively, from the expected values. At this point, it is worthwhile investigating what $A_{1,2'}$ value would arise using this new value for b. Letting $A_{1,2'} = (p^2 + 2s^2)/k$, when a and b have the same sign

$$A_{1,2'} = 146.0 \text{ km mol}^{-1}.$$

This value is only 5.1% larger than the reported one. Thus, the b value obtained in this calculation seems quite good: within a 5.1% correction on $A_{1,2'}$, all the reported intensities for SiD_3H are consistent. Moreover, according to both G and F sum rules, the reported intensities for all three molecules are consistent. It was also confirmed that a and b may not display opposite signs because, in this case, a 188.6 km mol^{-1} value would have been obtained for $A_{1,2'}$. This value is 36% larger than the reported one, and its assumption would destroy consistency with SiH_4 and SiD_4 intensity values, according to the G and F sum rules.

A third calculation was performed, supposing

$$(p^2 + 2s^2) = kA_{1,2'}$$

and

$$(q^2 + 2r^2) = kA_{3,4}.$$

This system of two quadratic equations converges to two solutions:

$$|a| = 0.317\ e \text{ amu}^{-1/2}$$

and

$$|b| = 0.382\ e \text{ amu}^{-1/2}$$

when a and b have the same sign, and

$$|a| = 0.275\ e \text{ amu}^{-1/2}$$

and

$$|b| = 0.368\ e \text{ amu}^{-1/2}$$

when a and b have opposite signs. Within a 4.4% variation in the reported A_2 value, which may be due to experimental error, the first solution is equivalent to the one already obtained in the second calculation. However, in the second calculation a and b are not allowed to have different signs, while this new calculation shows that changing the a value to 0.275 e amu$^{-1/2}$ would permit differing signs without changing $A_{1,2'}$, $A_{3,4}$, and $A_{3'}$, within the experimental error. Assuming this opposite sign solution, F and G sum rule consistency with the other two molecules is so astonishingly good that such an agreement seems fortuitous. The G sum rule agreement with the expected value is about 0.4% and the F sum rule value is about the very mean between the SiH_4 and SiD_4 values. Even though the A_2 value is 27.7% smaller than the reported one, casting this opposite sign solution in disfavor, both solutions of this third calculation have been considered. In Table I, the calculated values corresponding to these two solutions are compared with the reported ones. The last solution was not ruled out at this point because more evidence about a and b relative signs is desirable. F and G sum rule results are included in Table I.

TABLE I. Calculated and reported values for SiD_3H, intensities (Km mol^{-1}).

	Calculated		Reported[a]
	Same sign for a and b	Opposite sign for a and b	
A_2	97.8	74.0	102.3
$A_{3'}$	142.2	132.1	···
$A_{1,2'}$	138.8	138.9	138.9
$A_{3,4}$	138.7	138.0	138.6
			Expected values[b]
$\sum_i A_i$	517.5	483.0	481
$\sum_i A_i w_i^{-2}$	54.27	52.35	52.0 (cm^3 mol^{-1})

[a] Intensities from Ref. 10 and harmonic frequencies from Ref. 9.

[b] Obtained from SiH_4 and SiD_4 intensity data. See text.

Both $a^2/k = A_2$ and $b^2/k = A_{3'}$ intensity values have been presented in Ref. 9, allowing the calculation of the

$$(p^2 + 2s^2) = kA_{1,2'}$$

and

$$(q^2 + 2r^2) = kA_{3,4}$$

values. Considering the same sign for a and b, the calculated values of $A_{1,2'}$ and $A_{3,4}$ are 95.64 and 161.37 Km mol^{-1}, respectively. Using opposite signs for a and b, $A_{1,2'} = 134.06$ and

$$A_{3,4} = 170.72 \text{ Km mol}^{-1},$$

while the experimental values are 127.86 and 98.28 Km mol^{-1}, respectively. Thus, the symmetry of the SiD_3H molecule shows that the Ref. 9 intensity data for this molecule are inconsistent with the reported force field: the $A_{1,2'}$ value differs by 25% from the experimental one when a and b have the same sign and by 5% when a and b have opposite signs, but the $A_{3,4}$ values differ by more than 64% from the experimental value in both cases.

RESULTS

$\mathbf{P}_S$ matrices for all possible sign combinations of the $\mathbf{P}_Q$ elements for SiH_4, SiD_4, and the solution of SiD_3H in Table I which presents the same sign for a and b, were compared. For each molecule, one $\mathbf{P}_S$ matrix appeared which could be clearly distinguished as the closest one to one of the $\mathbf{P}_S$ matrices for each of the other two molecules. The differences among the elements of these three $\mathbf{P}_S$ matrices, one per molecule, are within a propagated 5% experimental error which has been assumed for the intensity values. Thus, preferred sign sets for the $\mathbf{P}_Q$ elements of the three molecules were established. The preferred $\mathbf{P}_S$ matrices and the corresponding $\mathbf{P}_Q$ element sign sets are related in Table II. In this table, two indicators of the degree if isotopic invariance have been included: the "distance"

$$D_{ij} = \left\{ \sum_{r=1}^{2} \left[(\partial p/\partial S_r)_i - (\partial p/\partial S_r)_j \right]^2 \right\}^{1/2}$$

between the sets of most probable values of the $\mathbf{P}_S$ elements for molecules i and j, and the

$$W_{ij} = \frac{\sum_{r=1}^{2} (W_r)_{ij}}{2}$$

mean overlap of the propagated experimental ranges of intensity errors (the propagated error does not include contributions from force field uncertainties). The minimal individ-

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ual W_r overlap was 5.7% of the propagated range of uncertainty, with 79.8% being the maximal one. Figure 1 presents a G sum rule visual display of the agreement among the selected sets of signs: each selected set corresponds to a most probable value for $\xi_{\mathrm{H,D}}$ and ξ_{Si}, represented by a point on the straight line of the corresponding molecule. The three points are very close to each other and within experimental error.

For the opposite sign solution for the SiD_3H intensities, there does not exist a $\mathbf{P}_S$ matrix for SiD_3H which is isotopically invariant with one of the $\mathbf{P}_S$ matrices for each SiH_4 and SiD_4. To obtain isotopic invariance, comparison of the data sets for SiH_4 and SiD_4 clearly indicates that all the elements of the $\mathbf{P}_Q$ matrix must have the same sign, both for SiH_4 and SiD_4. However, when these sign sets for SiH_4 and SiD_4 derivatives are compared with all the sign sets for the SiD_3H derivatives which correspond to the opposite sign solution in Table I, D_{ij} values higher than 0.35 e are found for the closest SiD_3H $\mathbf{P}_S$ matrix (about eighteen times as large as the maximal D_{ij} value of 0.019 e in Table II). This surely indicates that a and b must have equal signs.

For the Ref. 9 intensity data, the preferred $\mathbf{P}_S$ matrices correspond to opposite signs for the $\mathbf{P}_Q$ elements and are presented in Table III. Values for the SiD_3H molecule are not included because, as mentioned above, inconsistency among intensity and force field data prevents a meaningful use of the symmetry arguments to separate overlapped bands. Methods[7,8] using isotopic invariance and the G and F sum rules to separate bands may not be used either, because SiH_4 and SiD_4 intensity data are not precise enough. The F and G sum rule checks have already been discussed. The isotopic invariance test for preferred $\mathbf{P}_S$ matrices in Table III shows $D = 0.033\ e$, which is more than five times the D_{12} value in Table II, and a null W value, the error ranges not overlapping. Actually, the distance between the extremities of the two ranges of propagated experimental error has a dimension similar to that of the ranges themselves.

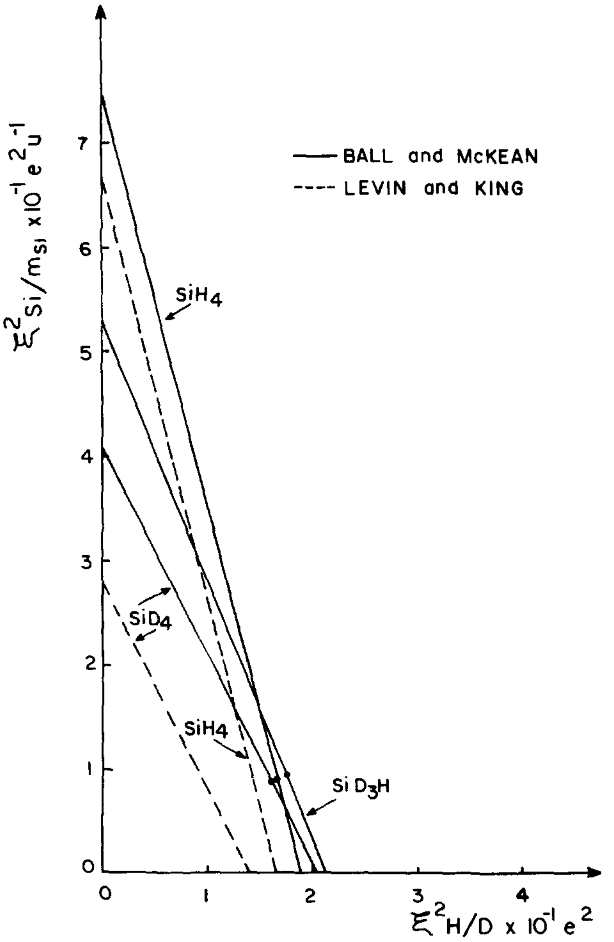

FIG. 1. G sum rule graphical test for silanes.

TABLE II. $\mathbf{P}_S$ matrices[a] (e).

		$SiH_4(1)$		$SiD_4(2)$	$SiD_3H(3)$
Stretching		− 0.354		− 0.350	− 0.367
Bending		− 0.219		− 0.215	− 0.223
D_{12}	W_{12}	D_{13}	W_{13}	D_{23}	W_{23}[b]
0.006	74.7	0.013	50.8	0.019	25.4

[a] All $\mathbf{P}_Q$ matrix elements are negative, according to CNDO calculations. Intensities are taken from Ref. 10, harmonic frequencies and force field from Ref. 9.

[b] See text for D_{ij} and W_{ij} symbols explanation. W_{ij} values are in %.

However, as a further sign check, quantum mechanical CNDO calculations of the $\mathbf{P}_Q$ matrix elements for SiH_4 were carried out. A calculated stretching derivative of − 0.17 e was obtained, while − 0.31 e was calculated for the bending derivative. The a and b values were also directly calculated by CNDO, yielding identical signs. The discrepancy in the A_2 intensity value in Table I, the F and G sum rules indications, the poor isotopic invariance and the CNDO results provide strong evidence for ruling out the opposite sign solution. The isotopically invariant atomic polar tensors and effective charges are listed in Table IV, as well as the band separation ratios for the SiD_3H overlapped bands. In this table, the hydrogen tensor third row and column refer to an axis along the molecular bond.

DISCUSSION

The 0.41 e hydrogen effective charge for silane in Table IV is a very high value when compared to values found for the hydrocarbons. The hydrocarbons investigated in Ref. 2 present hydrogen effective charge values below 0.19 e. This was confirmed in later works on the methanes[14] and other hydrocarbons.[6,15] The high value is comparable with those found for acetylene[2,6] (∼0.32 e) and hydrogen cyanide[16] (∼0.38 e). The silicon effective charge (1.59 e) is very high

TABLE III. $\mathbf{P}_S$ matrices[a] (e).

	SiH_4	SiD_4
Stretching	± 0.308	± 0.285
Bending	∓ 0.251	∓ 0.228
	$D = 0.033$	$W = 0.0$[b]

[a] Intensities, harmonic frequencies, and force field from Ref. 9.

[b] See text for D and W explanation.

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TABLE IV. Isotopically invariant polar tensors and effective charges[a] (e).

	Si			H		
	0.918	0	0	-0.189	0	0
$\mathbf{P}_X$	0	0.918	0	0	-0.189	0
	0	0	0.918	0	0	-0.308
ξ		1.59			0.410	
	Separation ratios for SiD_3H overlapped bands					
	$A_{2'}/A_1 = 6.28$			$A_3/A_4 = 1.22$		

[a] The mean values have been used. For hydrogen, -0.308 corresponds to stretching along the molecular bond. For silicon, the axes are the SiH_4 principal inertial ones. Signs are in accordance to CNDO calculations.

also, if compared to the carbon value in methane ($\sim 0.02\ e$). The silicon effective charge which corresponds to the interception of SiH_4 and SiD_4 lines in Fig. 1 is about 1.33 e, a value 16% smaller than the one in Table IV, which is obtained from polar tensors (it may be noted that silicon effective charges are 2.33 times more sensitive to intensity errors than carbon ones, because of the silicon–carbon mass ratio). In any case, both polar tensor and G sum rule values for ξ_{Si} are much higher than the ξ_{C} value encountered in methane. On the other hand, the G sum rule graph for SiH_4 and SiD_4 leads to a value of 0.41 e for ξ_{H}, in exact agreement with the polar tensor value.

Another interesting comparison of silane with the hydrocarbons involves the signs of the stretching and bending derivatives. The silane experimental data leads to the conclusion that both derivatives have the same sign and the CNDO results imply that the hydrogen end of the SiH bond becomes more negative for both SiH stretching and bending displacements. However, for hydrocarbons the hydrogen end of the CH bond is generally found to become more positive for CH bending displacements. Previous *ab initio* calculations also confirm that stretching and bending derivatives have the same sign in silanes,[17] consistent with the CNDO results.

CONCLUSIONS

The use of symmetry considerations in partially deuterated molecules has proved effective in separating overlapped bands and selecting the correct signs for dipole moment derivatives. The method may be easily expanded to molecules with a nonzero permanent dipole moment, by rotationally correcting the $\mathbf{P}_S$ elements. Perhaps an interesting feature is the dependence of the SiD_3H intensity values on the values of $\mathbf{L}^{-1}$ elements. It may be supposed that accurate intensity values for partially deuterated molecules can provide information about force fields. If so, perhaps it would be worthwhile measuring intensities for partially deuterated molecules, when there are doubts about the force field corresponding to a family of isotopically related molecules. Normally, intensity data for mixed hydrogen–deuterium molecules are relegated an importance inferior to the data corresponding to pure hydrogen or deuterium species, mainly because of the difficulty in separating overlapped bands by graphical methods. By taking advantage of symmetry properties, this band separation problem is minimized, allowing greater exploitation of vibrational intensity data.

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