

## The polar tensors, effective charges and separation ratios of overlapped bands in methanes

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**Abstract**—The separation ratios for the overlapped bands of CH<sub>3</sub>D, CD<sub>3</sub>H and CH<sub>2</sub>D<sub>2</sub> molecules have been obtained by a method based on the differences in molecular and electronic symmetry point groups. The signs of all the  $\partial P/\partial Q_i$  elements are established. Also, the atomic polar tensors and effective charges are calculated using the intensities of all five CH<sub>x</sub>D<sub>4-x</sub> molecules.

### INTRODUCTION

By the use of molecular symmetry properties, the fundamental overlapped bands of SiD<sub>3</sub>H gas phase in the i.r. spectra have been separated [1]. Also, the signs of the dipole moment derivatives have been found for this molecule and for the SiH<sub>4</sub> and SiD<sub>4</sub> molecules. Because neither severe physical nor mathematical approximations were employed, a separation ratio has been obtained which should be more accurate than the ratios obtained using graphical techniques. The method only depends on accurate experimental intensity data and the corresponding force fields. In this work, the overlapped bands of CH<sub>3</sub>D, CD<sub>3</sub>H and CH<sub>2</sub>D<sub>2</sub> molecules have been separated and the signs of the dipole moment derivatives have been found for these molecules and for CH<sub>4</sub> and CD<sub>4</sub>, using these symmetry properties. The results for the methanes are expected to be even more reliable than those for the silanes, because more accurate intensity data are available. Furthermore, the available data for the partially deuterated methanes involve three molecular species and not just one, as for the silanes. Such precision is important in determining the values of atomic polar tensors which are useful in transference to other molecules, in order to estimate i.r. intensities [2, 3].

### EXPERIMENTAL

Infrared intensity data for CH<sub>4</sub>, CD<sub>4</sub>, CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub> and CD<sub>3</sub>H have been reported by SAEKI *et al.* [4]. The molecular orientations are shown in Fig. 1. A 1.093 Å CH bond length is used [5]. Harmonic frequencies are taken from Ref. [6] and two force fields are used, one reported by SAEKI *et al.* [4] and the other by DUNCAN and MILLS [5]. Based on the reported intensities, an attempt is made to select the more accurate force field. Either one of the symmetry co-ordinate sets in Table 1 can be used in describing the normal modes of CH<sub>4</sub>(CD<sub>4</sub>), provided the molecule is properly oriented. *F* and *G* sum rules are taken from Ref. [7], except for the CD<sub>3</sub>H molecule, where  $\Sigma A_i/\omega_i^2$  and  $\Sigma A_i$  are considered to be  $22.8 \times 10^{-16}$  km<sup>3</sup>/mol and 57.35 km/mol, respectively.

### CALCULATIONS

Using the polar tensor method [8], the elements of the  $P_Q$  matrix,  $\partial P_\alpha/\partial Q_i$ , are directly related to the experimental data, within the biharmonic approximation. The  $3N - 6$  normal co-ordinates are related to the  $3N - 6$  internal symmetry co-ordinates, to produce a  $P_S$  matrix, whose elements are the dipole moment derivatives with respect to the symmetry co-ordinates,

$$P_S = P_Q L^{-1}, \quad (1)$$

where the *L* matrix is obtained by diagonalizing the

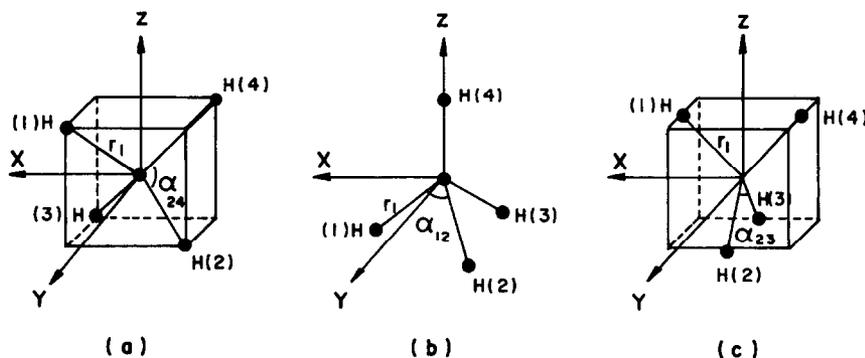


Fig. 1. Co-ordinate axes and molecular orientations for the methanes. (a) CH<sub>4</sub> and CD<sub>4</sub> molecules (*T<sub>d</sub>*). (b) CH<sub>3</sub>D and CD<sub>3</sub>H molecules (*C<sub>3v</sub>*). (c) CH<sub>2</sub>D<sub>2</sub> molecule (*C<sub>2v</sub>*).

Table 1. Symmetry co-ordinates

Species	<i>i</i>	<i>S<sub>i</sub></i>
CH <sub>3</sub> D; CD <sub>3</sub> H		
A <sub>1</sub>	1	(Δ <i>r</i> <sub>1</sub> + Δ <i>r</i> <sub>2</sub> + Δ <i>r</i> <sub>3</sub> + Δ <i>r</i> <sub>4</sub> )/2
	2	(3Δ <i>r</i> <sub>4</sub> - Δ <i>r</i> <sub>1</sub> - Δ <i>r</i> <sub>2</sub> - Δ <i>r</i> <sub>3</sub> )/√12
	3	(Δα <sub>12</sub> + Δα <sub>13</sub> + Δα <sub>23</sub> - Δα <sub>14</sub> - Δα <sub>24</sub> - Δα <sub>34</sub> ) <i>r</i> /√6
E	4	(2Δα <sub>23</sub> - Δα <sub>12</sub> - Δα <sub>13</sub> + 2Δα <sub>14</sub> - Δα <sub>24</sub> - Δα <sub>34</sub> ) <i>r</i> /√12
	5	(2Δ <i>r</i> <sub>1</sub> - Δ <i>r</i> <sub>2</sub> - Δ <i>r</i> <sub>3</sub> )/√6
	6	(2Δα <sub>23</sub> - Δα <sub>12</sub> - Δα <sub>13</sub> - 2Δα <sub>14</sub> + Δα <sub>24</sub> + Δα <sub>34</sub> ) <i>r</i> /√12
	7	(-Δα <sub>12</sub> + Δα <sub>13</sub> + Δα <sub>24</sub> - Δα <sub>34</sub> ) <i>r</i> /2
	8	(Δ <i>r</i> <sub>2</sub> - Δ <i>r</i> <sub>3</sub> )/√2
	9	(-Δα <sub>12</sub> + Δα <sub>13</sub> - Δα <sub>24</sub> + Δα <sub>34</sub> ) <i>r</i> /2
CH <sub>2</sub> D <sub>2</sub>		
A <sub>1</sub>	1	(Δ <i>r</i> <sub>1</sub> + Δ <i>r</i> <sub>2</sub> + Δ <i>r</i> <sub>3</sub> + Δ <i>r</i> <sub>4</sub> )/2
	2	(Δ <i>r</i> <sub>1</sub> - Δ <i>r</i> <sub>2</sub> - Δ <i>r</i> <sub>3</sub> + Δ <i>r</i> <sub>4</sub> )/2
	3	(Δα <sub>23</sub> - Δα <sub>14</sub> ) <i>r</i> /√2
	4	(2Δα <sub>23</sub> - Δα <sub>12</sub> - Δα <sub>13</sub> + 2Δα <sub>14</sub> - Δα <sub>24</sub> - Δα <sub>34</sub> ) <i>r</i> /√12
B <sub>1</sub>	5	(Δ <i>r</i> <sub>1</sub> - Δ <i>r</i> <sub>4</sub> )/√2
	6	(-Δα <sub>12</sub> - Δα <sub>13</sub> + Δα <sub>24</sub> + Δα <sub>34</sub> ) <i>r</i> /√2
A <sub>2</sub>	7	(-Δα <sub>12</sub> + Δα <sub>13</sub> + Δα <sub>24</sub> - Δα <sub>34</sub> ) <i>r</i> /2
B <sub>2</sub>	8	(Δ <i>r</i> <sub>2</sub> - Δ <i>r</i> <sub>3</sub> )/√2
	9	(-Δα <sub>12</sub> - Δα <sub>13</sub> - Δα <sub>24</sub> + Δα <sub>34</sub> ) <i>r</i> /2

symmetrized GF product. The symmetry co-ordinates can be related to the 3*N* space fixed Cartesian co-ordinates to obtain the molecular polar tensor

$$\mathbf{P}_X = \mathbf{P}_Q(\mathbf{L}^{-1}\mathbf{U}\mathbf{B}) + \mathbf{P}_\rho\beta, \quad (2)$$

which is the juxtaposition of the atomic polar tensors [8],  $\mathbf{P}_X^{(a)}$ .  $\mathbf{L}^{-1}\mathbf{U}\mathbf{B}$  is the transformation matrix between normal and Cartesian co-ordinates and the term  $\mathbf{P}\beta$  is the rotational correction, which depends on the atomic masses, molecular geometries and equilibrium dipole moments. For the molecules in this work, the permanent moments are zero and the rotational corrections are null.

The atomic effective charge,  $\xi_a$ , defined by King [9], can be expressed as

$$\xi_a^2 = \text{Tr}(\mathbf{P}_X^a \mathbf{P}_X^a). \quad (3)$$

$$\begin{bmatrix} 0 & 0 & 0 & \partial p_x/\partial Q_4 & \partial p_x/\partial Q_5 & \partial p_x/\partial Q_6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \partial p_y/\partial Q_7 & \partial p_y/\partial Q_8 & \partial p_y/\partial Q_9 \\ \partial p_z/\partial Q_1 & \partial p_z/\partial Q_2 & \partial p_z/\partial Q_3 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} = \mathbf{P}_Q \mathbf{L}^{-1}. \quad (4)$$

(1) CH<sub>3</sub>D

For both molecules CH<sub>3</sub>D and CD<sub>3</sub>H, the  $\mathbf{P}_Q$  matrix has the form

Both  $\xi_a$  and  $\mathbf{P}_X$  are isotopically invariant within the Born-Oppenheimer approximation. In addition, the permanent dipole moment is null and  $\mathbf{P}_S$  is also invariant under isotopic substitution. The molecular symmetry, which depends on the atomic masses, varies with isotopic substitution as does the  $\mathbf{P}_Q$  matrix. On the other hand, the  $\mathbf{P}_S$  matrix behavior reflects the electronic symmetry. Note that electronic and molecular symmetries are not the same for the partially deuterated molecules and the differences can be exploited to calculate the individual intensities of the overlapped vibrational bands of the partially deuterated species. The experimental data and Eqn. (1)

Substituting the numerical values of the  $\mathbf{L}$  matrix, the two sets of equations are obtained for both force fields:

DUNCAN and MILLS force field

$$\begin{aligned} \partial p_z/\partial Q_1 &= 0.003738\ell + 0.524157a \\ \partial p_z/\partial Q_2 &= 0.094231\ell - 0.620554a \\ \partial p_z/\partial Q_3 &= 1.221586\ell + 0.015675a \\ \partial p_x/\partial Q_4 &= 0.521279\ell - 0.001616a \\ \partial p_x/\partial Q_5 &= a \\ \partial p_x/\partial Q_6 &= \ell \end{aligned}$$

SAEKI *et al.* force field

$$\begin{aligned} \partial p_z/\partial Q_1 &= -0.007895\ell + 0.551811a \\ \partial p_z/\partial Q_2 &= 0.152484\ell - 0.599273a \end{aligned}$$

$$\begin{aligned}\partial p_x/\partial Q_3 &= 1.212917\ell + 0.026557a \\ \partial p_x/\partial Q_4 &= 0.520194\ell + 0.000539a \\ \partial p_x/\partial Q_5 &= a \\ \partial p_x/\partial Q_6 &= \ell.\end{aligned}$$

From the experimental values,  $(\partial p_x/\partial Q_2)^2 = A_2/K$ ,  $(\partial p_x/\partial Q_1)^2 + 2(\partial p_x/\partial Q_5)^2 = A_{1,5}/K$  and  $(\partial p_x/\partial Q_3)^2 + 2(\partial p_x/\partial Q_4)^2 + 2(\partial p_x/\partial Q_6)^2 = A_{3,4,6}/K$ . The system of equations is solved, first by taking  $A_{1,5}$  and  $A_{3,4,6}$  as known quantities and solution I, for  $a$  and  $\ell$ , is obtained. The following possibilities exist:  $a$  and  $\ell$  are of the same or opposite signs. If  $a$  and  $\ell$  have the same sign, then  $a = \pm 0.715664$  and  $\ell = \pm 0.425736$  ( $D/\text{\AA}$ ) a.m.u.<sup>-1/2</sup> for the DUNCAN and MILLS force field and  $a = \pm 0.712193$  and  $\ell = \pm 0.424224$  ( $D/\text{\AA}$ ) a.m.u.<sup>-1/2</sup> for the SAEKI *et al.* force field. If  $a$  and  $\ell$  have opposite signs, then  $a = \pm 0.716403$  and  $\ell = \pm 0.431933$  for the DUNCAN and MILLS force field and  $a = \pm 0.710566$  and  $\ell = \pm 0.435845$  ( $D/\text{\AA}$ ) a.m.u.<sup>-1/2</sup> for the SAEKI *et al.* force field. A second (and third) set of calculations was performed using  $A_2$ , where all the  $\partial p/\partial Q_i$  are taken as a function of  $\ell$  and  $A_{1,5}(A_{3,4,6})$ , in order to obtain the value of  $\ell$ . These results correspond to solutions II and III. The alternative results are  $\ell = \pm 0.696275$  and  $a = \pm 0.715430$  ( $D/\text{\AA}$ ) a.m.u.<sup>-1/2</sup> for solution II, and  $\ell = \pm 0.425918$  and  $a = \pm 0.674376$  ( $D/\text{\AA}$ ) a.m.u.<sup>-1/2</sup> for solution III. These values are obtained by the use of the DUNCAN and MILLS force field. The values obtained from SAEKI's force field are very close to these. Table 2 contains the calculated and experimental intensities, the  $F$  and  $G$  sum rule results. Note that the calculated values for  $A_2$ , when  $a$  and  $\ell$  have opposite signs, is of the order of 60% higher than the experimental value, so this possibility can be ruled out. Comparing the experimental value  $A_{3,4,6}$  with the one calculated from solution II, we see that it is extremely high, so that solution II can be discarded. Although solution I with  $a$  and  $\ell$  having the same sign differs slightly from solution III, the separation ratios for the overlapped bands are the same:

$$\begin{aligned}\text{DUNCAN and MILLS force field} \\ A_1 : A_5 &= 1.0 : 7.2 \\ A_3 : A_4 : A_6 &= 2.9 : 1.0 : 3.7\end{aligned}$$

$$\begin{aligned}\text{SAEKI } et al. \text{ force field} \\ A_1 : A_5 &= 1.0 : 6.7 \\ A_3 : A_4 : A_6 &= 2.9 : 1.0 : 3.7.\end{aligned}$$

Observe that both sets of results are in good agreement.

## (2) CD<sub>3</sub>H

By substitution of the respective  $L_{ij}$  values in Eqn. (4), and knowing that the  $P_Q$  matrix has the same form as the one for the CH<sub>3</sub>D molecule, the following sets of equations are obtained:

$$\begin{aligned}\text{DUNCAN and MILLS force field} \\ \partial p_x/\partial Q_1 &= 0.384778a + 0.063210\ell \\ \partial p_x/\partial Q_2 &= a \\ \partial p_x/\partial Q_3 &= \ell \\ \partial p_x/\partial Q_4 &= -0.008725a + 0.751947\ell \\ \partial p_x/\partial Q_5 &= 0.844324a + 0.110191\ell \\ \partial p_x/\partial Q_6 &= -0.011298a + 0.828955\ell \\ \text{SAEKI } et al. \text{ force field} \\ \partial p_x/\partial Q_1 &= 0.347135a + 0.078318\ell \\ \partial p_x/\partial Q_2 &= a \\ \partial p_x/\partial Q_3 &= \ell \\ \partial p_x/\partial Q_4 &= -0.016707a + 0.735849\ell \\ \partial p_x/\partial Q_5 &= 0.835095a + 0.154269\ell \\ \partial p_x/\partial Q_6 &= -0.014234a + 0.835626\ell.\end{aligned}$$

Using the reported intensities,  $(\partial p_x/\partial Q_1)^2 + 2(\partial p_x/\partial Q_5)^2 = A_{1,5}/K$ ,  $(\partial p_x/\partial Q_2)^2 = A_2/K$ ,  $2(\partial p_x/\partial Q_4)^2 = A_4/K$  and  $(\partial p_x/\partial Q_3)^2 + 2(\partial p_x/\partial Q_6)^2 = A_{3,6}/K$ , and the above equations, values for  $a$  and  $\ell$  can be calculated in the following way. Considering as known quantities the reported values of  $A_{1,5}$  and  $A_{3,6}$ ,  $A_2$  and  $A_{3,6}$ ,  $A_4$  and  $A_4$ , and  $A_{1,5}$  and  $A_4$ , four sets of solutions, I, II, III, and IV, respectively, are obtained for  $a$  and  $\ell$ . Note that the two alternatives,  $A_2$  and  $A_{1,5}$ , and  $A_{3,6}$  and  $A_4$  have not been included since the corresponding values obtained for  $\ell$  are extremely poor. This can be seen by taking the value of  $a$ , obtained from the  $A_2$  intensity and substituting in the equation for  $\partial p_x/\partial Q_1$ . As the numerical coefficient for  $\ell$  in this equation is very small, the propagated error in  $\ell$  is large and the values obtained for the calculated intensities are poor.

Table 2. Calculated and experimental intensities (km/mol) and  $G$  and  $F$  ( $\times 10^{-16}$  km<sup>3</sup>/mol) sum rule results for the CH<sub>3</sub>D molecule

	Duncan and Mills [5] F.F.			Solution III	Saeki <i>et al.</i> [4] F.F.		Exp. int. [4]
	Solution I ( $a > 0$ ; $\ell > 0$ )	Solution II ( $a > 0$ ; $\ell < 0$ )			Solution I ( $a > 0$ ; $\ell > 0$ )	Solution I ( $a > 0$ ; $\ell < 0$ )	
$A_1$	6.00	5.91	6.06	5.33	6.42	6.61	49.29*
$A_2$	6.90	9.95	6.05	6.05	5.54	10.24	6.05
$A_3$	11.93	11.27	31.39	11.91	12.03	10.98	31.37†
$A_4$	4.12	4.32	11.06	4.12	4.13	4.33	†
$A_5$	43.29	43.38	43.26	38.44	42.88	42.66	*
$A_6$	15.32	15.77	40.77	15.34	15.2	16.06	†
$\Sigma A_i$	87.56	90.6	138.77	81.19	86.2	90.88	86.7
$\Sigma A_i/\omega_i^2$	25.35	25.97	56.79	24.63	25.07	26.08	23.2

\*Intensity value of the superimposed bands  $A_1 + A_5$ .

†Intensity value of the superimposed bands  $A_3 + A_4 + A_6$ .

Using the same criterion as used for CH<sub>3</sub>D, it can be seen that  $a$  and  $\ell$  here should have opposite signs. So, the separation ratio of the overlapped bands for solution sets I-IV are

$$\begin{aligned}\partial p_x/\partial Q_6 &= 0.017227a + 0.882668\ell \\ \partial p_y/\partial Q_8 &= 0.740942a + 0.088514\ell \\ \partial p_y/\partial Q_9 &= \ell\end{aligned}$$

solution I				
$A_1:A_5$	1.0:10.09	1.0:10.08	1.0:10.06	1.0:10.07
$A_3:A_6$	1.0:1.43	1.0:1.44	1.0:1.44	1.0:1.44
for the DUNCAN and MILLS force field and				
$A_1:A_5$	1.0:12.23	1.0:12.26	1.0:12.24	1.0:12.22
$A_3:A_6$	1.0:1.478	1.0:1.478	1.0:1.478	1.0:1.478

for the SAEKI *et al.* force field. See Table 3 for the calculated and experimental intensities, and the  $G$  and  $F$  sum rule results.

### (3) CH<sub>2</sub>D<sub>2</sub>

Since the CH<sub>2</sub>D<sub>2</sub> molecule belongs to the  $C_{2v}$  point group (remember that the electronic symmetry is  $T_d$ ), the symmetry co-ordinates are not the same as those used for the  $C_{3v}$  symmetry molecules (see Table 1). The  $P_Q$  matrix also has a slightly different form

### SAEKI *et al.* force field

$$\begin{aligned}\partial p_x/\partial Q_1 &= 0.463541a + 0.102615\ell \\ \partial p_x/\partial Q_2 &= 0.751003a + 0.005721\ell \\ \partial p_x/\partial Q_3 &= 0.011098a + 0.694198\ell \\ \partial p_x/\partial Q_4 &= 0.005315a + 0.642222\ell \\ \partial p_x/\partial Q_5 &= a \\ \partial p_x/\partial Q_6 &= 0.026635a + 0.889505\ell \\ \partial p_y/\partial Q_8 &= 0.746717a + 0.138757\ell \\ \partial p_y/\partial Q_9 &= \ell.\end{aligned}$$

$$\begin{bmatrix} 0 & 0 & 0 & \partial p_x/\partial Q_5 & \partial p_x/\partial Q_6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \partial p_y/\partial Q_7 & \partial p_y/\partial Q_8 & \partial p_y/\partial Q_9 \\ \partial p_z/\partial Q_1 & \partial p_z/\partial Q_2 & \partial p_z/\partial Q_3 & \partial p_z/\partial Q_4 & 0 & 0 & 0 & 0 \end{bmatrix}.$$

The molecule presents nine non-degenerate normal modes of vibration, of which one is not i.r. active. The following equations have been obtained by the use of Eqn. (4):

$$\begin{aligned}\text{DUNCAN and MILLS force field} \\ \partial p_x/\partial Q_1 &= 0.493145a + 0.069015\ell \\ \partial p_x/\partial Q_2 &= 0.728943a + 0.003227\ell \\ \partial p_x/\partial Q_3 &= 0.005517a + 0.688065\ell \\ \partial p_x/\partial Q_4 &= 0.007794a + 0.644497\ell \\ \partial p_x/\partial Q_5 &= a\end{aligned}$$

By the use of the above equations plus the reported intensities  $(\partial p_x/\partial Q_1)^2 + (\partial p_y/\partial Q_8)^2 = A_{1,8}/K$ ,  $(\partial p_x/\partial Q_2)^2 + (\partial p_x/\partial Q_5)^2 = A_{2,5}/K$  and  $(\partial p_x/\partial Q_3)^2 + (\partial p_x/\partial Q_4)^2 + (\partial p_x/\partial Q_6)^2 + (\partial p_y/\partial Q_9)^2 = A_{3,4,6,9}/K$ , two possible solution sets, I and II, are obtained. For solution I the experimental intensities of  $A_{3,4,6,9}$  and  $A_{2,5}$  are used; for solution II those of  $A_{1,8}$  and  $A_{3,4,6,9}$ . The third option, involving  $A_{2,5}$  and  $A_{1,8}$ , has been abandoned since the coefficients are large for  $a$  and small for  $\ell$ , and it is not possible to obtain the  $\ell$  values with fair

Table 3. Calculated and experimental intensities (km/mol) for the CD<sub>3</sub>H molecule and  $G$  and  $F$  ( $\times 10^{-16}$  km<sup>3</sup>/mol) sum rule results ( $a$  and  $\ell$  have opposite signs)

Solution:	Duncan and Mills [5] F.F.				Saeki <i>et al.</i> [4] F.F.				Exp. int. [4]
	I	II	III	IV	I	II	III	IV	
$A_1$	1.823	1.884	1.9	1.826	1.528	1.41	1.42	1.53	20.22*
$A_2$	15.311	15.77	15.77	15.23	16.9	15.77	15.77	16.82	15.77
$A_3$	6.046	6.044	5.65	5.65	5.94	5.95	5.69	5.679	14.72†
$A_4$	7.092	7.094	6.64	6.64	6.935	6.92	6.64	6.64	6.64
$A_5$	18.396	18.998	19.11	18.394	18.69	17.28	17.38	18.69	*
$A_6$	8.674	8.676	8.12	8.12	8.78	8.772	8.41	8.4	†
$\Sigma A_i$	57.34	58.47	57.2	55.86	58.77	56.10	55.32	57.76	57.35
$\Sigma A_i/\omega_i^2$	22.7	22.88	21.78	21.58	22.78	22.37	21.66	22.01	22.76

\*Experimental value for  $A_1 + A_5$ .

†Experimental value for  $A_3 + A_6$ .

accuracy. The calculations show that  $\alpha$  and  $\beta$  should have opposite signs. Table 4 contains the calculated and experimental intensities. The following separation ratios for the overlapped bands has been obtained for the DUNCAN and MILLS force field.

	solution I	solution II
$A_1:A_8$	1.0:2.33	1.0:2.33
$A_2:A_5$	1.0:1.87	1.0:1.87
$A_3:A_4:A_6:A_9$	1.15:1.0:1.83:2.5	1.15:1.0:1.84:2.49,
and, for the SAEKI <i>et al.</i> force field		
$A_1:A_8$	1.0:2.75	1.0:2.74
$A_2:A_5$	1.0:1.79	1.0:1.79
$A_3:A_4:A_6:A_9$	1.14:1.0:1.8:2.48	1.14:1.0:1.79:2.49.

matrices and the corresponding  $P_Q$  element sign sets are given. CNDO/2 calculations were performed and the respective signs for the stretching and bending derivatives are negative and positive. For the signs in

### DISCUSSION

Once the separation ratios of the overlapped fundamental bands have been obtained for the partially deuterated molecules, the  $P_S$  matrices can be calculated for all possible sign combinations of the  $P_Q$  matrix elements and the isotopically invariant  $P_S$  matrices can be chosen (see Ref. [1] for the criteria used to indicate the degree of isotopic invariance). In this way, the preferred sign sets for the  $P_Q$  elements of the five molecules are established. In Table 5, the invariant  $P_S$

agreement with the CNDO/2 calculations, the atomic polar tensors (average of the five tensors obtained from  $CH_4$ ,  $CD_4$ ,  $CH_3D$ ,  $CD_3H$  and  $CH_2D_2$  intensities) and effective charges has been calculated, and are presented in Table 6. The CNDO/2 calculations indicate that the net charges on the hydrogen atoms are small in magnitude, but positive in the equilibrium position. Using the negative  $\partial p_z/\partial z$  element which is associated with the bond stretching co-ordinate indicates a redistribution of the electronic charge away from the

Table 4. Calculated and experimental intensities for the  $CH_2D_2$  molecule (km/mol) and  $G$  and  $F$  ( $\times 10^{-16}$  km<sup>3</sup>/mol) sum rule results ( $\alpha$  and  $\beta$  with opposite signs)

	Duncan and Mills [5] F.F.		Saeki <i>et al.</i> [4] F.F.		Exp. int. [4]
	Solution I	Solution II	Solution I	Solution II	
$A_1$	4.314	4.16	3.297	3.705	13.85*
$A_2$	11.59	11.213	11.914	13.169	33.26†
$A_3$	4.645	4.644	4.64	4.638	26.10‡
$A_4$	4.026	4.026	4.063	4.065	‡
$A_5$	21.67	20.97	21.346	23.585	‡
$A_6$	7.384	7.39	7.305	7.289	‡
$A_8$	10.042	9.69	9.055	10.145	*
$A_9$	10.046	10.04	10.092	10.111	‡
$\Sigma A_i$	73.72	72.13	71.71	76.7	73.2
$\Sigma A_i/\omega_i^2$	24.05	23.85	23.65	24.28	23.11

\* Experimental value for  $A_1 + A_8$ .

† Experimental value for  $A_2 + A_5$ .

‡ Experimental value for  $A_3 + A_4 + A_6 + A_9$ .

Table 5.  $P_S$  matrices (e) for the methanes

	$CH_4$	$CD_4$	$CH_3D$	$CD_3H$	$CH_2D_2$
		Duncan and Mills [5] force field			
Stretching	$\pm 0.156$	$\pm 0.155$	$\pm 0.154$	$\pm 0.150$	$\pm 0.154$
Bending	$\pm 0.076$	$\pm 0.072$	$\pm 0.069$	$\pm 0.069$	$\pm 0.071$
		Saeki <i>et al.</i> [4] force field			
Stretching	$\pm 0.161$	$\pm 0.159$	$\pm 0.158$	$\pm 0.153$	$\pm 0.155$
Bending	$\pm 0.071$	$\pm 0.067$	$\pm 0.069$	$\pm 0.064$	$\pm 0.067$

Table 6. Atomic polar tensors and effective charges\* of the methanes

Duncan and Mills F.F.			Saeki <i>et al.</i> F.F.		
$\mathbf{P}_X^{(C)} = \begin{bmatrix} 0.011 & 0 & 0 \\ 0 & 0.011 & 0 \\ 0 & 0 & 0.011 \end{bmatrix}$			$\mathbf{P}_X^{(C)} = \begin{bmatrix} 0.026 & 0 & 0 \\ 0 & 0.026 & 0 \\ 0 & 0 & 0.026 \end{bmatrix}$		
$\mathbf{P}_X^{(H)} = \begin{bmatrix} 0.062 & 0 & 0 \\ 0 & 0.062 & 0 \\ 0 & 0 & -0.133 \end{bmatrix}$			$\mathbf{P}_X^{(H)} = \begin{bmatrix} 0.046 & 0 & 0 \\ 0 & 0.046 & 0 \\ 0 & 0 & -0.136 \end{bmatrix}$		
$\xi_C = 0.02; \xi_H = 0.16$			$\xi_C = 0.04; \xi_H = 0.16$		

\*The mean values have been used. For hydrogen, the  $\partial p_x/\partial z$  elements correspond to stretching along the molecular bond. For carbon, the axes are the  $\text{CH}_4$  principal inertial ones. Signs are in agreement with the CNDO calculations.

carbon atom. The first two elements,  $\partial p_x/\partial x$  and  $\partial p_y/\partial y$ , are very small in magnitude, showing that the charge flux for these bending movements is negligible. Recently another set of i.r. intensities has been reported by BODE and SMIT [10], for  $\text{CH}_4$  and  $\text{CD}_4$ . Using their reported data and the DUNCAN and MILLS force field [5], the atomic polar tensors, invariant  $\mathbf{P}_S$  matrices and effective charges have been calculated. These values are almost identical to those for the  $\text{CH}_3\text{D}$ ,  $\text{CD}_3\text{H}$  and  $\text{CH}_2\text{D}_2$  molecules given in Table 5.

The results from Table 5 can also be compared with several semiempirical and *ab initio* MO calculations [11–14] reported in the literature, where the signs of dipole moment derivatives have been found to be identical to those obtained in this work. The good agreement between our results in Table 6 and the *ab initio* ones [14, 15] can also be noted.

Comparing the atomic polar tensors, the effective charges and the intensity separation ratios for the two force fields, it may be seen that the results are much the same. Thus, we cannot choose between these force fields.

In conclusion, from the use of this separation method for the overlapped bands of partially deuterated molecules, one can obtain the signs of the  $\mathbf{P}_Q$  matrices' elements for these molecules and a good estimation of the polar tensors and the effective charges of the hydrogen and carbon atoms, since five isotopically related molecules have been used rather than two, as was done before [14]. These values are reliable enough to be used in the transference to other molecules for which the prediction of i.r. intensities are desired.

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#### REFERENCES

- [1] M. M. C. FERREIRA and A. B. M. S. BASSI, *J. chem. Phys.* **81**, 6 (1984).
- [2] W. B. PERSON, in *Vibrational Intensities in Infrared and Raman Spectroscopy* (edited by W. B. PERSON and G. ZERBI). Elsevier, Amsterdam (1982).
- [3] R. E. BRUNS, Y. HASE and I. M. BRINN, *J. phys. Chem.* **84**, 3593 (1980).
- [4] S. SAEKI, M. MIZUNO and S. KONDO, *Spectrochim. Acta* **32A**, 403 (1976).
- [5] J. L. DUNCAN and I. M. MILLS, *Spectrochim. Acta* **20**, 523 (1964).
- [6] J. HEICKLEN, *Spectrochim. Acta* **17**, 201 (1961), with the exception of the  $\text{CH}_2\text{D}_2$  molecule which has been taken from L. M. SVERDLOV, M. A. KOVNER and E. P. KRAJNOV, *Vibrational Spectra of Polyatomic Molecules*. John Wiley, New York (1974).
- [7] B. B. NETO and R. E. BRUNS, *J. chem. Phys.* **69**, 4147 (1978).
- [8] W. B. PERSON and J. H. NEWTON, *J. chem. Phys.* **61**, 1040 (1974).
- [9] W. T. KING, G. B. MAST and P. P. BLANCHETE, *J. chem. Phys.* **56**, 4440 (1972).
- [10] J. H. G. BODE and W. M. A. SMIT, *J. phys. Chem.* **84**, 198 (1980).
- [11] G. A. SEGAL and M. L. KLEIN, *J. chem. Phys.* **47**, 4236 (1967).
- [12] S. KONDO and S. SAEKI, *Spectrochim. Acta* **29A**, 735 (1973).
- [13] W. MEYER and P. PULAY, *J. chem. Phys.* **56**, 2109 (1972).
- [14] J. H. NEWTON and W. B. PERSON, *J. phys. Chem.* **82**, 226 (1978).
- [15] P. LAZZERETTI and R. ZANASI, *J. chem. Phys.* **84**, 3916 (1986).