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

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(Received 17 October 1986; in final form 22 March 1987; accepted 22 March 1987)

Abstract—The separation ratios for the overlapped bands of \( \text{CH}_3\text{D} \), \( \text{CD}_3\text{H} \) and \( \text{CH}_2\text{D}_2 \) molecules have been obtained by a method based on the differences in molecular and electronic symmetry point groups. The signs of all the \( \frac{\partial P}{\partial Q_i} \) elements are established. Also, the atomic polar tensors and effective charges are calculated using the intensities of all five \( \text{CH}_x\text{D}_{4-x} \) molecules.

INTRODUCTION

By the use of molecular symmetry properties, the fundamental overlapped bands of \( \text{SiD}_3\text{H} \) 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 \( \text{SiH}_4 \) and \( \text{SiD}_4 \) 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 \( \text{CH}_3\text{D} \), \( \text{CD}_3\text{H} \) and \( \text{CH}_2\text{D}_2 \) molecules have been separated and the signs of the dipole moment derivatives have been found for these molecules and for \( \text{CH}_4 \) and \( \text{CD}_4 \), 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 \( \text{CH}_4 \), \( \text{CD}_4 \), \( \text{CH}_3\text{D} \), \( \text{CH}_2\text{D}_2 \) and \( \text{CD}_3\text{H} \) 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 \( \text{CH}_x\text{D}_{4-x} \), provided the molecule is properly oriented. \( F \) and \( G \) sum rules are taken from Ref. [7], except for the \( \text{CD}_3\text{H} \) molecule, where \( \Sigma l_l/Q_l^2 \) and \( \Sigma A_l \) are considered to be \( 2.28 \times 10^{-16} \) km/mol and 57.35 km/mol, respectively.

CALCULATIONS

Using the polar tensor method [8], the elements of the \( \mathbf{P}_Q \) matrix, \( \frac{\partial P_l}{\partial Q_i} \), 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 \( \nu \)-vibrations, to produce a \( \mathbf{P}_S \) matrix, whose elements are the dipole moment derivatives with respect to the symmetry co-ordinates,

\[
\mathbf{P}_S = \mathbf{P}_Q \mathbf{L}^{-1},
\]

where the \( \mathbf{L} \) matrix is obtained by diagonalizing the

![Fig. 1. Co-ordinate axes and molecular orientations for the methanes. (a) \( \text{CH}_4 \) and \( \text{CD}_4 \) molecules (\( T_d \)). (b) \( \text{CH}_3\text{D} \) and \( \text{CD}_3\text{H} \) molecules (\( C_{3h} \)). (c) \( \text{CH}_2\text{D}_2 \) molecule (\( C_{2v} \)).](image-url)
Table 1. Symmetry co-ordinates

<table>
<thead>
<tr>
<th>Species i</th>
<th>( S_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>((\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)/2)</td>
</tr>
<tr>
<td>A_2</td>
<td>((3\Delta r_4 - \Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{12})</td>
</tr>
<tr>
<td>E</td>
<td>((\Delta s_{23} + \Delta s_{12} - \Delta s_{13} + \Delta s_{24} - \Delta s_{24} + \Delta s_{34} - \Delta s_{34})/\sqrt{6})</td>
</tr>
<tr>
<td>B_1</td>
<td>((2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6})</td>
</tr>
<tr>
<td>B_2</td>
<td>((2\Delta s_{23} - \Delta s_{12} - \Delta s_{13} - \Delta s_{24} + \Delta s_{24} + \Delta s_{34})/\sqrt{12})</td>
</tr>
<tr>
<td>A_3</td>
<td>((- \Delta s_{12} + \Delta s_{13} + \Delta s_{24} + \Delta s_{34})/2)</td>
</tr>
</tbody>
</table>

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

\[ P_X = P_0(L \cdot U \cdot B) + P_\rho \beta, \] (2)

which is the juxtaposition of the atomic polar tensors [8], \( P_0 \) is the transformation matrix between normal and Cartesian co-ordinates and the term \( P_\beta \) 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, \( \xi_i \), defined by King [9], can be expressed as

\[ \xi_i^2 = Tr(P_i^e P_i^e). \] (3)

Both \( \xi_i \) and \( P_i^e \) are isotopically invariant under the Born–Oppenheimer approximation. In addition, the permanent dipole moment is null and \( P_i^e \) is also invariant under isotopic substitution. The molecular symmetry, which depends on the atomic masses, varies with isotopic substitution as does the \( P_i^e \) matrix. On the other hand, the \( P_i^e \) 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) can be used to obtain the separation ratios of the overlapped bands and the relative signs of all \( \partial p_i/\partial Q_j \).

The isotopically invariant polar tensors and the effective charges are also obtained with greater precision, since five isotopically related molecules can be used instead of just CH_4 and CD_4.

Using Eqn. (1) and the defined symmetry co-
 ordinates and Cartesian axes, one can write for all five molecules

\[ \begin{bmatrix}
0 & 0 & 0 & 0 & X & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & X & Y \\
0 & X & Y & 0 & 0 & 0 & 0 & 0 
\end{bmatrix} = P_0 L^{-1}. \] (4)

(1) CH_3D

For both molecules CH_3D and CD_3H, the \( P_0 \) matrix has the form

\[ \begin{bmatrix}
0 & 0 & 0 & \partial p_i/\partial Q_1 & \partial p_i/\partial Q_2 & \partial p_i/\partial Q_3 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \partial p_i/\partial Q_1 & \partial p_i/\partial Q_2 & \partial p_i/\partial Q_3 & 0 & 0 \\
\end{bmatrix} \]

Substituting the numerical values of the \( L \) matrix, the two sets of equations are obtained for both force fields:

**Duncan and Mills force field**

- \( \partial p_i/\partial Q_1 = 0.0037386 + 0.524157a \)
- \( \partial p_i/\partial Q_2 = 0.0942316 - 0.620554a \)
- \( \partial p_i/\partial Q_3 = 1.2251866 + 0.001175a \)
- \( \partial p_i/\partial Q_4 = 0.5212796 - 0.001616a \)
- \( \partial p_i/\partial Q_5 = 0.1524846 - 0.599273a \)

**Saeki et al. force field**

- \( \partial p_i/\partial Q_1 = -0.0078956 + 0.551811a \)
- \( \partial p_i/\partial Q_2 = 0.1524846 - 0.599273a \)
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\[ \frac{\partial p_x}{\partial Q_3} = 1.2129174 + 0.026557a \]
\[ \frac{\partial p_y}{\partial Q_4} = 0.520194 + 0.00539a \]
\[ \frac{\partial p_z}{\partial Q_5} = a \]
\[ \frac{\partial p_y}{\partial Q_6} = \delta. \]

From the experimental values, \((\partial p_x/\partial Q_3)^2 = A_2/K, \) \((\partial p_y/\partial Q_4)^2 + 2(\partial p_z/\partial Q_5)^2 = A_{1.5}/K \) and \((\partial p_z/\partial Q_6)^2 - A_{2.6}/K. \) The system of equations is solved, first by taking \(a, 1.5 \) and \(A_{2.6} \) as known quantities and solution I, for \(a, 1.5, \) is obtained. The following possibilities exist: \(a, \delta \) are of the same or opposite signs. If \(a, \delta \) have the same signs, then \(a = \pm 0.715664 \) and \(\delta = \pm 0.425736 \) \((D/A) \) a.m.u. -1/2 for the DUNCAN and MILLS force field and \(a = \pm 0.712193 \) and \(\delta = \pm 0.435845 \) \((D/A) \) a.m.u. -1/2 for the SAEKI et al. force field. If \(a, \delta \) have opposite signs, then \(a = \pm 0.716403 \) and \(\delta = \pm 0.431933 \) for the DUNCAN and MILLS force field and \(a = \pm 0.710566 \) and \(\delta = \pm 0.435845 \) \((D/A) \) a.m.u. -1/2 for the SAEKI et al. force field. A second (and third) set of calculations was performed using \(A_{1.5} \), where all the \(\partial p_x/\partial Q_3 \) are taken as a function of \(\delta \) and \(A_{1.5}(A_{2.6}) \), in order to obtain the value of \(\delta \). These results correspond to solutions II and III. The alternative results are \(\delta = \pm 0.696275 \) and \(\delta = \pm 0.424224 \) \((D/A) \) a.m.u. -1/2 for solution II, and \(\delta = \pm 0.433918 \) and \(\delta = \pm 0.674376 \) \((D/A) \) a.m.u. -1/2 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 \(A_{2.6} \), when \(a, \delta \) have different signs, is of the order of 60% higher than the experimental value, so this possibility can be ruled out.

Comparing the experimental value \(A_{2.6} \) 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 \(a, \delta \) having the same sign differs slightly from solution III, the separation ratios for the overlapped bands are the same:

**DUNCAN and MILLS force field**

\[ A_1 : A_2 = 1.0 : 7.2 \]
\[ A_3 : A_4 : A_6 = 2.9 : 1.0 : 3.7 \]

**SAEKI et al. force field**

\[ A_1 : A_2 = 1.0 : 6.7 \]
\[ A_3 : A_4 : A_6 = 2.9 : 1.0 : 3.7 \]

Observe that both sets of results are in good agreement.

(2) \text{CD}_3\text{H}

By substitution of the respective \(L_{ij} \) values in Eqn (4), and knowing that the \(P_{ij} \) matrix has the same form as the one for the \(\text{CH}_3\text{D} \) molecule, the following sets of equations are obtained:

**DUNCAN and MILLS force field**

\[ \frac{\partial p_x}{\partial Q_1} = 0.384778a + 0.063210 \]
\[ \frac{\partial p_y}{\partial Q_2} = a \]
\[ \frac{\partial p_z}{\partial Q_3} = \delta \]

Using the reported intensities, \((\partial p_x/\partial Q_1)^2 + 2(\partial p_z/\partial Q_3)^2 = A_{1.5}/K, \) \((\partial p_y/\partial Q_2)^2 = A_{2.6}/K, \) \((\partial p_z/\partial Q_4)^2 + 2(\partial p_p/\partial Q_5)^2 = A_{2.6}, \) and the above equations, values for \(a, \delta \) can be calculated in the following way. Considering as known quantities the reported values of \(A_{1.5} \) and \(A_{2.6} \), the values obtained for the calculated intensities are poor. This can be seen by taking the value of \(a, \delta \), obtained from the \(2, 3, 4 \) intensity and substituting in the equation for \(\partial p_x/\partial Q_1 \). As the numerical coefficient for \(\delta \) in this equation is very small, the propagated error in \(\delta \) is large and the value obtained for the calculated intensities are poor.

**SAEKI et al. force field**

<table>
<thead>
<tr>
<th>A,</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A6</th>
<th>ΣA, ΣA/</th>
<th>a,Q</th>
<th>ΣA/4Ωa</th>
<th>Exp. int. [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>6.00</td>
<td>5.91</td>
<td>6.06</td>
<td>5.33</td>
<td>6.42</td>
<td>6.61</td>
<td>49.29*</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>6.90</td>
<td>9.95</td>
<td>6.05</td>
<td>6.05</td>
<td>5.54</td>
<td>10.24</td>
<td>6.05</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>11.93</td>
<td>11.27</td>
<td>31.39</td>
<td>11.04</td>
<td>12.03</td>
<td>16.06</td>
<td>31.37†</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>4.12</td>
<td>4.32</td>
<td>11.06</td>
<td>4.12</td>
<td>4.13</td>
<td>4.32</td>
<td>4.32</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>43.29</td>
<td>43.38</td>
<td>43.26</td>
<td>38.44</td>
<td>42.88</td>
<td>42.66</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>15.77</td>
<td>15.77</td>
<td>40.77</td>
<td>15.34</td>
<td>15.2</td>
<td>16.06</td>
<td>†</td>
<td></td>
</tr>
<tr>
<td>ΣA</td>
<td>87.56</td>
<td>90.6</td>
<td>138.77</td>
<td>81.19</td>
<td>86.2</td>
<td>90.88</td>
<td>86.7</td>
<td></td>
</tr>
<tr>
<td>ΣA/4Ωa</td>
<td>25.35</td>
<td>25.97</td>
<td>56.79</td>
<td>24.63</td>
<td>25.07</td>
<td>26.08</td>
<td>23.2</td>
<td></td>
</tr>
</tbody>
</table>

*Intensity value of the superimposed bands \(A_1 + A_2 \).
†Intensity value of the superimposed bands \(A_3 + A_4 + A_6 \).
Using the same criterion as used for \( \text{CH}_3\text{D} \), it can be seen that \( a \) and \( b \) here should have opposite signs. So, the separation ratio of the overlapped bands for solution sets I–IV are

<table>
<thead>
<tr>
<th>Solution</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1:A_5 )</td>
<td>1.0:10.09</td>
<td>1.0:10.08</td>
<td>1.0:10.06</td>
<td>1.0:10.07</td>
</tr>
<tr>
<td>( A_3:A_6 )</td>
<td>1.0:1.43</td>
<td>1.0:1.44</td>
<td>1.0:1.44</td>
<td>1.0:1.44</td>
</tr>
</tbody>
</table>

for the Duncan and Mills force field and

<table>
<thead>
<tr>
<th>Solution</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1:A_5 )</td>
<td>1.0:12.23</td>
<td>1.0:12.26</td>
<td>1.0:12.24</td>
<td>1.0:12.22</td>
</tr>
<tr>
<td>( A_3:A_6 )</td>
<td>1.0:1.478</td>
<td>1.0:1.478</td>
<td>1.0:1.478</td>
<td>1.0:1.478</td>
</tr>
</tbody>
</table>

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) \( \text{CH}_2\text{D}_2 \)

Since the \( \text{CH}_2\text{D}_2 \) 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 \( P_0 \) matrix also has a slightly different form

\[
\begin{bmatrix}
0 & 0 & 0 & \partial p_x/\partial Q_4 \\
0 & 0 & 0 & 0 \\
\partial p_x/\partial Q_1 & \partial p_x/\partial Q_2 & \partial p_x/\partial Q_3 & \partial p_x/\partial Q_4 & 0 \\
\end{bmatrix}
\]

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):

**Duncan and Mills force field**

\[
\begin{align*}
\partial p_x/\partial Q_1 &= 0.493145a + 0.069015b \\
\partial p_x/\partial Q_2 &= 0.728943a + 0.003227b \\
\partial p_x/\partial Q_3 &= 0.005517a + 0.688065b \\
\partial p_x/\partial Q_4 &= 0.007794a + 0.644976b \\
\partial p_x/\partial Q_5 &= a \\
\end{align*}
\]

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

**SAEKI et al. force field**

\[
\begin{align*}
\partial p_x/\partial Q_1 &= 0.463541a + 0.102615G \\
\partial p_x/\partial Q_2 &= 0.751003a + 0.005721~ \\
\partial p_x/\partial Q_3 &= 0.011098a + 0.6941986 \\
\partial p_x/\partial Q_4 &= 0.005315a + 0.6422226 \\
\partial p_x/\partial Q_5 &= a \\
\end{align*}
\]

Table 3. Calculated and experimental intensities (km/mol) for the \( \text{CD}_3\text{H} \) molecule and \( G \) and \( F \) sum rule results (\( a \) and \( G \) have opposite signs)

<table>
<thead>
<tr>
<th>Solution:</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>Exp. int. [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1.823</td>
<td>1.884</td>
<td>1.9</td>
<td>1.826</td>
<td>1.528</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>15.311</td>
<td>15.77</td>
<td>15.77</td>
<td>15.23</td>
<td>16.9</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>6.046</td>
<td>6.044</td>
<td>5.65</td>
<td>5.65</td>
<td>5.94</td>
</tr>
<tr>
<td>( A_4 )</td>
<td>7.092</td>
<td>7.094</td>
<td>6.64</td>
<td>6.64</td>
<td>6.935</td>
</tr>
<tr>
<td>( A_5 )</td>
<td>18.396</td>
<td>18.998</td>
<td>19.11</td>
<td>18.394</td>
<td>18.69</td>
</tr>
<tr>
<td>( A_6 )</td>
<td>8.674</td>
<td>8.676</td>
<td>8.12</td>
<td>8.12</td>
<td>8.78</td>
</tr>
<tr>
<td>( \Sigma A_4/\alpha )</td>
<td>57.34</td>
<td>58.47</td>
<td>57.2</td>
<td>55.86</td>
<td>58.77</td>
</tr>
<tr>
<td>( \Sigma A_4/\alpha )</td>
<td>22.7</td>
<td>22.88</td>
<td>21.78</td>
<td>21.58</td>
<td>22.78</td>
</tr>
</tbody>
</table>

*Experimental value for \( A_1 + A_5 \).
†Experimental value for \( A_3 + A_6 \).
The polar tensors, effective charges and separation ratios of overlapped bands in methanes

accuracy. The calculations show that \( \sigma \) and \( \delta \) 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.

<table>
<thead>
<tr>
<th></th>
<th>Solution I</th>
<th>Solution II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 : A_8 )</td>
<td>1.0 : 2.33</td>
<td>1.0 : 2.33</td>
</tr>
<tr>
<td>( A_2 : A_9 )</td>
<td>1.0 : 1.87</td>
<td>1.0 : 1.87</td>
</tr>
<tr>
<td>( A_3 : A_4 : A_5 : A_8 )</td>
<td>1.15 : 1.0 : 1.83 : 2.5</td>
<td>1.15 : 1.0 : 1.84 : 2.49</td>
</tr>
</tbody>
</table>

and, for the SAEKI et al. force field

<table>
<thead>
<tr>
<th></th>
<th>Solution I</th>
<th>Solution II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 : A_8 )</td>
<td>1.0 : 2.75</td>
<td>1.0 : 2.74</td>
</tr>
<tr>
<td>( A_2 : A_9 )</td>
<td>1.0 : 1.79</td>
<td>1.0 : 1.79</td>
</tr>
<tr>
<td>( A_3 : A_4 : A_5 : A_8 )</td>
<td>1.14 : 1.0 : 1.8 : 2.48</td>
<td>1.14 : 1.0 : 1.79 : 2.49</td>
</tr>
</tbody>
</table>

**DISCUSSION**

Once the separation ratios of the overlapped fundamental bands have been obtained for the partially deuterated molecules, the \( P_m \) matrices can be calculated for all possible sign combinations of the \( P_q \) matrix elements and the isotopically invariant \( P_m \) 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 \( P_S \) 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 agreement with the CNDO/2 calculations, the atomic polar tensors (average of the five tensors obtained from CH\(_4\), CD\(_4\), CH\(_3\)D, CD\(_3\)H and CH\(_2\)D\(_2\) 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 \( \partial n / \partial z \) 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\(_3\)D\(_2\) molecule (km/mol) and \( G \) and \( F \) (\( \times 10^{-16} \) km\(^2\)/mol) sum rule results (\( \sigma \) and \( \delta \) with opposite signs)

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<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution I</td>
<td>Solution II</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>4.314</td>
<td>4.16</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>11.59</td>
<td>11.213</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>4.645</td>
<td>4.644</td>
</tr>
<tr>
<td>( A_4 )</td>
<td>4.026</td>
<td>4.026</td>
</tr>
<tr>
<td>( A_5 )</td>
<td>21.67</td>
<td>20.97</td>
</tr>
<tr>
<td>( A_6 )</td>
<td>7.384</td>
<td>7.39</td>
</tr>
<tr>
<td>( A_8 )</td>
<td>10.042</td>
<td>9.69</td>
</tr>
<tr>
<td>( A_9 )</td>
<td>10.046</td>
<td>10.04</td>
</tr>
<tr>
<td>( \Sigma A_i )</td>
<td>73.72</td>
<td>72.13</td>
</tr>
<tr>
<td>( \Sigma A_{ij} )</td>
<td>24.05</td>
<td>23.85</td>
</tr>
</tbody>
</table>

*Experimental value for \( A_1 + A_8 \).
†Experimental value for \( A_2 + A_3 \).
‡Experimental value for \( A_3 + A_4 + A_5 + A_8 \).

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

<table>
<thead>
<tr>
<th></th>
<th>CH(_4)</th>
<th>CD(_4)</th>
<th>CH(_3)D</th>
<th>CD(_3)H</th>
<th>CH(_2)D(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td>±0.156</td>
<td>±0.153</td>
<td>±0.154</td>
<td>±0.150</td>
<td>±0.154</td>
</tr>
<tr>
<td>Bending</td>
<td>±0.076</td>
<td>±0.072</td>
<td>±0.069</td>
<td>±0.069</td>
<td>±0.071</td>
</tr>
</tbody>
</table>

Duncan and Mills [5] force field

<table>
<thead>
<tr>
<th></th>
<th>CH(_4)</th>
<th>CD(_4)</th>
<th>CH(_3)D</th>
<th>CD(_3)H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td>±0.161</td>
<td>±0.159</td>
<td>±0.158</td>
<td>±0.153</td>
</tr>
<tr>
<td>Bending</td>
<td>±0.071</td>
<td>±0.067</td>
<td>±0.069</td>
<td>±0.064</td>
</tr>
</tbody>
</table>

Saeki et al. [4] force field

<table>
<thead>
<tr>
<th></th>
<th>CH(_4)</th>
<th>CD(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td>±0.161</td>
<td>±0.159</td>
</tr>
<tr>
<td>Bending</td>
<td>±0.071</td>
<td>±0.067</td>
</tr>
</tbody>
</table>
Table 6. Atomic polar tensors and effective charges* of the methanes

<table>
<thead>
<tr>
<th>Duncan and Mills F.F.</th>
<th>Saeki et al. F.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbf{P}_x^{(C)} = \begin{bmatrix} 0.011 &amp; 0 &amp; 0 \ 0 &amp; 0.011 &amp; 0 \ 0 &amp; 0 &amp; 0.011 \end{bmatrix}$</td>
<td>$\mathbf{P}_x^{(C)} = \begin{bmatrix} 0.026 &amp; 0 &amp; 0 \ 0 &amp; 0.026 &amp; 0 \ 0 &amp; 0 &amp; 0.026 \end{bmatrix}$</td>
</tr>
<tr>
<td>$\mathbf{P}_x^{(H)} = \begin{bmatrix} 0.062 &amp; 0 &amp; 0 \ 0 &amp; 0.062 &amp; 0 \ 0 &amp; 0 &amp; -0.133 \end{bmatrix}$</td>
<td>$\mathbf{P}_x^{(H)} = \begin{bmatrix} 0.046 &amp; 0 &amp; 0 \ 0 &amp; 0.046 &amp; 0 \ 0 &amp; 0 &amp; -0.136 \end{bmatrix}$</td>
</tr>
</tbody>
</table>

$\xi_C = 0.02; \quad \xi_H = 0.16$

$\xi_C = 0.04; \quad \xi_H = 0.16$

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

carbon atom. The first two elements, $\partial \mathbf{P}_x / \partial x$ and $\partial \mathbf{P}_y / \partial y$, 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 CH$_4$ and CD$_4$. Using their reported data and the DUNCAN and MILLS force field [5], the atomic polar tensors, invariant $\mathbf{P}_x$ matrices and effective charges have been calculated. These values are almost identical to those for the CH$_3$D, CD$_3$H and CH$_2$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 $\mathbf{P}_x$ 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.

Acknowledgements—We are grateful Prof. ROY E. BRUNS for his suggestions and discussions, CNPq for a fellowship to M.M.C.F and the Centro de Computação da Unicamp for computer time.

REFERENCES