Transformation of *ab initio* force fields on going to a set of redundant vibrational coordinates in tetrahedral molecular fragments

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Abstract

The valence force fields of methane and methanol molecules computed using the quantum-chemical GAMESS package with a set of independent vibrational coordinates in the approximations B3LYP/acc-pVQZ and B3LYP/6-311G**, respectively, have been transformed to a set of redundant vibrational coordinates. It has been shown that the use of the transformed fields enables one to represent in full the initial frequencies of normal molecular vibrations, establishing the field symmetry and making the forms of normal vibrations more adequate and clear.

Keywords: Force fields; Vibrational spectra; Sets of independent and redundant vibrational coordinates

1. Introduction

Molecular force fields are still of particular interest to researchers as parameters greatly determine some physical, chemical, and spectral properties of the molecules. The banks of empirical force constants created in the sixties - seventies of the last century [1,2] are presently extensively increased due to numerous nonempirical quantum-chemical computations of molecular force fields [3-5] and improved approaches to the computations of empirical fields. [6,7]. Correlation of the results obtained during various computations may involve difficulties because sets of independent or redundant coordinates are used and the vibrational coordinates in use are too diversified (natural, Cartesian, by the Yury-Bradley method). Note that empirical force fields are, as a rule, computed for a set of the redundant natural vibrational coordinates, whereas nonempirical force fields are more often computed using a set of the independent natural coordinates. In the latter case a force field gives no indication of a molecular symmetry and transfering of its elements to more complex molecules is difficult. As is well-known, force fields derived for a set of the redundant natural coordinates are free from the above limitations, completely reflecting a molecular symmetry. Such fields may be easily transferred to the allied molecules. Because of this, finding of a force field for a set of the redundant coordinates based on the force constant matrix for a set of the independent coordinates is a very interesting challenge. Denoting a matrix of force constants for a set of the redundant natural coordinates by K and the corresponding matrix for a set of the independent coordinates by k, we can state that, provided K is known, the matrix k may be always found unambiguously as soon as the matrix A expressing the redundant coordinates in terms of the independent ones is found [8]. An inverse problem for a planar molecular fragment having three valence angles with the common vertex is solved in paper [9]. At the same time, among the fragments including redundant coordinates, the tetrahedral fragment, where six valence angles have a common vertex, is widely encountered. This work presents the possibility for the above-mentioned transformations of force fields for the methane and methanol molecules containing a regular and a slightly deformed tetrahedral fragment.

2. Computational method

Optimization of the geometry and computations of force fields for the methane and methanol molecules have been realized with the use of the quantum-chemical GAMESS package (VERSION = 1 OCT 2010 (R3)) [10] in the approximations B3LYP/acc-pVQZ and B3LYP/6-311G** with allowances for T_d and C_S symmetries. In both cases OPTOL=10^{-7}. After the definition of the form for A matrix, the force fields derived for a set of independent vibrational coordinates have been recalculated for a complete set of the redundant coordinates with the help of matrix equations [9]. Normal modes of the molecules of CH_4 and CH_3COH were computed with the derived force fields using the package [11].
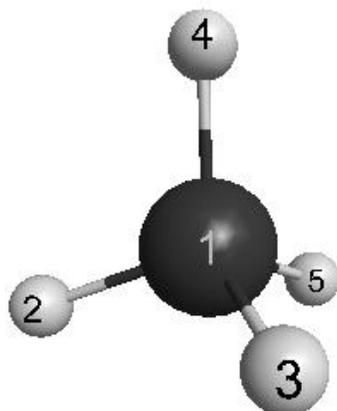
Figure 1. Methane molecule with numbering of atoms.

3. CH$_4$ force fields

Figure 1 presents a molecule of methane.

Nine independent (q_i) and ten redundant (Q_i) coordinates are introduced as follows:

$$\delta l_{C_1H_2} \Leftrightarrow q_1, Q_1; \qquad \delta l_{C_1H_3} \Leftrightarrow q_2, Q_2;$$
$$\delta l_{C_1H_4} \Leftrightarrow q_3, Q_3; \qquad \delta l_{C_1H_5} \Leftrightarrow q_4, Q_4;$$
$$\delta \varphi_{H_3C_1H_2} \Leftrightarrow q_5, Q_5;$$
$$\delta \varphi_{H_4C_1H_2} \Leftrightarrow q_6, Q_6; \qquad \delta \varphi_{H_5C_1H_2} \Leftrightarrow q_7, Q_7;$$
$$\delta \varphi_{H_3C_1H_4} \Leftrightarrow q_8, Q_8; \qquad \delta \varphi_{H_5C_1H_3} \Leftrightarrow q_9, Q_9;$$
$$\delta \varphi_{H_4C_1H_5} \Leftrightarrow Q_{10}.$$

Let us consider a part of the matrix of force constants that is associated with the valence angles H-C-H. As the interactions of the angles with a common vertex and a side (e.g., Q_5 and Q_6) and of those with a common vertex only (e.g., Q_5 and Q_{10}) are physically distinct, in the general case this matrix takes the form

$$
\begin{array}{ccccccc}
Q & Q_5 & Q_6 & Q_7 & Q_8 & Q_9 & Q_{10} \\
Q_5 & \alpha & \beta & \beta & \beta & \beta & \gamma \\
Q_6 & \beta & \alpha & \beta & \beta & \gamma & \beta \\
Q_7 & \beta & \beta & \alpha & \gamma & \beta & \beta \\
Q_8 & \beta & \beta & \gamma & \alpha & \beta & \beta \\
Q_9 & \beta & \gamma & \beta & \beta & \alpha & \beta \\
Q_{10} & \gamma & \beta & \beta & \beta & \beta & \alpha
\end{array} \Rightarrow
$$

$$
K = \begin{pmatrix}
\alpha & \beta & \beta & \beta & \beta & \gamma \\
\beta & \alpha & \beta & \beta & \gamma & \beta \\
\beta & \beta & \alpha & \gamma & \beta & \beta \\
\beta & \beta & \gamma & \alpha & \beta & \beta \\
\beta & \gamma & \beta & \beta & \alpha & \beta \\
\gamma & \beta & \beta & \beta & \beta & \alpha
\end{pmatrix} \qquad (1)
$$

Indeed, despite the fact that the coordinates Q_5 - Q_{10} are equivalent necessarily requiring the equality of the corresponding diagonal constants $K_{ii} = \alpha$, $i \in (5-10)$, nondiagonal force constants are divided into two nonoverlapping subsets due to the symmetry elements of T$_d$ group. Specifically, the constants $K_{5,10}; K_{6,9}; K_{7,8}$ and their symmetric analogues are transformed only into each other under the effect of any symmetry operation. Since the components of any physical quantities are invariant with respect to the transformations caused by symmetry operations we have ($K_{5,10} = K_{6,9} = K_{7,8} = \gamma$). The second subset is formed by the remaining nondiagonal force constants for which the above is valid ($K_{5,6} = K_{5,7} = \cdots = \beta$). The form of the matrix A is determined from the condition:

$$Q_5 + Q_6 + Q_7 + Q_8 + Q_9 = -Q_{10} \qquad (2)$$

In this case A takes the form:

$$
A = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1 \\
-1 & -1 & -1 & -1 & -1
\end{pmatrix} \qquad (3)
$$

Next we can compute this part of a force field in independent coordinates [8] as follows:

$$k = \tilde{A}KA \qquad (4)$$

Performing the transformations, we have:

$$
k = \begin{pmatrix}
2\alpha - 2\gamma & \alpha - \gamma & \alpha - \gamma & \alpha - \gamma & \alpha - \gamma \\
\alpha - \gamma & 2\alpha - 2\beta & \alpha - \beta & \alpha - \beta & \alpha + \gamma - 2\beta \\
\alpha - \gamma & \alpha - \beta & 2\alpha - 2\beta & \alpha + \gamma - 2\beta & \alpha - \beta \\
\alpha - \gamma & \alpha - \beta & \alpha + \gamma - 2\beta & 2\alpha - 2\beta & \alpha - \beta \\
\alpha - \gamma & \alpha + \gamma - 2\beta & \alpha - \beta & \alpha - \beta & 2\alpha - 2\beta
\end{pmatrix}
$$
$$(5)$$

As seen, the use of a set of independent coordinates leads to the nonequal diagonal force constants for the five physically equivalent angles H-C-H, and the value $k_{55} = 2\alpha - 2\gamma$ of a diagonal force constant for the valence angle q_5 loosing its pair Q_{10} turns to be distinct from the remaining four ($2\alpha - 2\beta$). Besides, instead of two (β, γ) differing nondiagonal force constants, we have three ($\alpha - \gamma$, $\alpha - \beta$, $\alpha + \gamma - 2\beta$) and hence $k_{5,6} = \alpha - \gamma$, $k_{6,7} = \alpha - \beta$. Since $\gamma \neq \beta$, we have $k_{5,6} \neq k_{6,7}$.

Table 1. Force field of methane for sets of independent and redundant coordinates.

Coordinate number	Coordinate number					
	q_5/Q_5	q_6/Q_6	q_7/Q_7	q_8/Q_8	q_9/Q_9	Q_{10}
q_5/Q_5	1.4027/ 0.602					
q_6/Q_6	0.7014/ −0.1256	1.4552/ 0.602				
q_7/Q_7	0.7014/ −0.1256	0.7276/ −0.1256	1.4552/ 0.602			
q_8/Q_8	0.7014/ −0.1256	0.7276/ −0.1256	0.7538/ −0.0995	1.4552/ 0.602		
q_9/Q_9	0.7014/ −0.1256	0.7538/ −0.0995	0.7276/ −0.1256	0.7276/ −0.1256	1.4552/ 0.602	
Q_{10}	−0.0995	−0.1256	−0.1256	−0.1256	−0.1256	0.602

But we can show that, due to the effect of C_3 operation involving the atoms H_2-C_1, $k_{5,6}$ becomes $k_{6,7}$ and hence they must be equal. In this way with the use of independent coordinates a force field is not following T_d symmetry. The pseudoinverse matrix A^{-1} is of the form:

$$A^{-1} = \frac{1}{6}\begin{pmatrix} 5 & -1 & -1 & -1 & -1 & -1 \\ -1 & 5 & -1 & -1 & -1 & -1 \\ -1 & -1 & 5 & -1 & -1 & -1 \\ -1 & -1 & -1 & 5 & -1 & -1 \\ -1 & -1 & -1 & -1 & 5 & -1 \end{pmatrix} \quad (6)$$

Using the relation $K = \tilde{A}^{-1}kA^{-1}$ [9], we can get K:

$$K = \frac{1}{6}\begin{pmatrix} 5\alpha-4\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha-4\beta+5\gamma \\ -\alpha+2\beta-\gamma & 5\alpha-4\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha-4\beta+5\gamma & -\alpha+2\beta-\gamma \\ -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & 5\alpha-4\beta-\gamma & -\alpha-4\beta+5\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma \\ -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha-4\beta+5\gamma & 5\alpha-4\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma \\ -\alpha+2\beta-\gamma & -\alpha-4\beta+5\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & 5\alpha-4\beta-\gamma & -\alpha+2\beta-\gamma \\ -\alpha-4\beta+5\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & -\alpha+2\beta-\gamma & 5\alpha-4\beta-\gamma \end{pmatrix} (7)$$

Comparing (7) and (1), we should require that:

$$\frac{5}{6}\alpha - \frac{4}{6}\beta - \frac{1}{6}\gamma = \alpha \implies \gamma = -4\beta - \alpha \quad (8)$$

and substitute γ into (7), in this case the matrix K takes the from of (1). It is clear that for its description we need two (α, β) rather than three parameters:

$$K = \begin{pmatrix} \alpha & \beta & \beta & \beta & \beta & -4\beta-\alpha \\ \beta & \alpha & \beta & \beta & -4\beta-\alpha & \beta \\ \beta & \beta & \alpha & -4\beta-\alpha & \beta & \beta \\ \beta & \beta & -4\beta-\alpha & \alpha & \beta & \beta \\ \beta & -4\beta-\alpha & \beta & \beta & \alpha & \beta \\ -4\beta-\alpha & \beta & \beta & \beta & \beta & \alpha \end{pmatrix}$$
$$(9)$$

Then the matrix k may be also written in a more simple form as:

$$k = \begin{pmatrix} 4\alpha+8\beta & 2\alpha+4\beta & 2\alpha+4\beta & 2\alpha+4\beta & 2\alpha+4\beta \\ 2\alpha+4\beta & 2\alpha-2\beta & \alpha-\beta & \alpha-\beta & -6\beta \\ 2\alpha+4\beta & \alpha-\beta & 2\alpha-2\beta & -6\beta & \alpha-\beta \\ 2\alpha+4\beta & \alpha-\beta & -6\beta & 2\alpha-2\beta & \alpha-\beta \\ 2\alpha+4\beta & -6\beta & \alpha-\beta & \alpha-\beta & 2\alpha-2\beta \end{pmatrix}$$
$$(10)$$

Let us find how all the foregoing meets the computational results for a force field of a methane molecule in the approximation B3LYP/acc-pVQZ using the above program package [10]. The values of force constants for the considered coordinates in units of 10^6 cm^{-2} are listed in Table 1 (unless otherwise specified, all values of the force constants in the text and in the Tables are given in these units). Correlating (10) and the values indicated in Table 1, we can find:

$$-6\beta = 0.7538 \implies \beta = -0.12563$$
$$(11)$$

$$2\alpha - 2\beta = 1.4552 \implies 2\alpha + 0.25126 = 1.4552 \implies$$
$$\alpha = 0.602 \implies \gamma = -0.09948 \quad (12)$$

We can easily verify that after substitution of (11) and (12) into (10) we get the force constants with the values listed in Table 1 and with minor errors which are inevitable in the process of numerical quantum-chemical computations of force fields. Next we recalculate the elements of a force field (Table 1) for a set of the redundant coordinates with the use of the relation $K = \tilde{A}^{-1}kA^{-1}$.

A similar result may be obtained if we substitute (11) and (12) into (1). The values of the diagonal and nondiagonal force constants for the bonds C-H and their interactions $k_{11} = k_{22} = k_{33} = k_{44}$ and k_{ij}, where $j > i$ and $i \in (1,2,3)$, $j \in (2,3,4)$, remain unaltered (k_{11} =8.306; $k_{12} = k_{13} = k_{14} \cdots = k_{34} = 0.0568$), whereas those of the coupling constants for the bonds and angles are varied. The coupling constant value of

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Table 2. Calculated wave numbers and normal modes of methane.

Harmonic wave numbers[*]	Independent coordinates		Redundant coordinates	
ω (cm^{-1})	Wave numbers (cm^{-1})	Normal modes	Wave numbers (cm^{-1})	Normal modes
1358	1348.41	$1.14q_5$	1348.55	$-1.057Q_6+1.057Q_9$
1358	1348.42	$-1.14q_6+1.14q_9$	1348.56	$1.054Q_7-1.054Q_8$
1358	1348.45	$1.14q_7+1.14q_8$	1348.58	$1.14Q_5 -1.14Q_{10}$
1567	1565.28	$+1.03q_7+1.03q_8$	1565.19	$-0.99Q_6+0.77Q_7+0.77Q_8-0.99Q_9$
1567	1565.32	$0.97q_5-0.80q_6-0.17q_7-0.17q_8-0.80q_9$	1565.21	$1.02Q_5-0.32Q_6-0.70Q_7-0.70Q_8-0.32Q_9+1.02Q_{10}$
3027	3024.78	$0.51q_1+0.51q_2+0.51q_3+0.51q_4$	3024.75	$0.51Q_1+0.51Q_2+0.51Q_3+0.51Q_4$
3158	3131.54	$-0.49q_1+0.61q_2-0.60q_3+0.48q_4$	3131.54	$0.52Q_1-0.52Q_2+0.53Q_3-0.52Q_4$
3158	3131.54	$-0.61q_1-0.48q_2+0.50q_3+0.59q_4$	3131.54	$0.50Q_1+0.54Q_2-0.50Q_3-0.54Q_4$
3158	3131.56	$0.53q_1-0.55q_2-0.54q_3+0.56q_4$	3131.56	$-0.55Q_1+0.50Q_2+0.54Q_3-0.49Q_4$

[*]According to [15]

the bond C-H and of the angle H-C-H is equal to 0.0997 when a common bond is available and to -0.0997 when there is no common bond. Then we can correlate the values of empirical and nonempirical force fields for a methane molecule. To illustrate, the values $K_{11} = 9.3313$ and $K_{12} = 0.2106$ seem to be somewhat overestimated in [12,13]. In paper [14] these constants are in line with the values obtained in this work ($K_{11} = 8.34 \pm 0.03$; $K_{12} = 0.05 \pm 0.01$). An agreement with other force constants is slightly worse ($K_{55} = 0.71 \pm 0.03$; $K_{16} = 0.35 \pm 0.05$; $K_{56} = -0.035 \pm 0.005$), probably due to the selection of a somewhat simplified form of the potential energy:

$$U= \frac{1}{2}K_q\sum_i q_i^2 + h\sum_{ij} q_iq_j + a\sum_{ij} q_i\alpha_j + \frac{1}{2}K_\alpha\sum_i \alpha_i^2 + l\sum_{ij}\alpha_i\alpha_j \tag{13}$$

Correlation with the data given in [15] is not very correct as there the force constants are given for the symmetry coordinates. Nevertheless, we can take F_{11} and F_{33}, which are respectively equal to 5.4388 and 5.3704 mdyne/Å, as analogues of K_{11} in a good agreement with the value $K_{11}=5.3241$ mdyne/Å derived in this work. The values of F_{22} and F_{44}, respectively equal to 0.486 and 0.4576 mdyne/rad, are taken as analogues of K_{55}, whereas in this work the value for K_{55} equals 0.4585 mdyne/rad. A single coupling constant for the bond and angle in the block of F_2 symmetry equals -0.1880 mdyne ·

Å/rad^2, and being correlated to K_{18} =-0.0696 mdyne · Å/rad^2 reveals a considerable difference. It is seen that some empirical and nonempirical force constants of a methane molecule are close in their values. Now let us consider a correlation between the wave numbers and normal modes with the use of the force fields given in Table 1. The correlation data are listed in Table 2.

As seen, the force field computed for a set of the redundant coordinates makes it possible to reproduce the wave numbers obtained in the initial quantum-chemical computations. And with the use of the redundant coordinates, the normal modes reveal symmetry of vibrations to a greater degree. In both cases there is a satisfactory agreement between the computed and harmonic [15] vibrational wave numbers (ω) of a methane molecule.

4. CH$_3$OH force fields

In a molecule of methanol (Figure 2), due to a lower symmetry level as compared to methane, from T_d to C_S the angles between C-O and C-H bonds
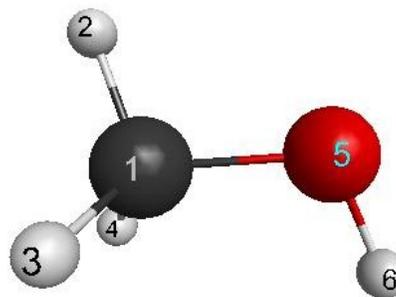
Figure 2. Methanol molecule with numbering of atoms.

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Table 3. Force field of methanol for sets of independent and redundant coordinates.

Coordinate number	Coordinate number					
	q_6/Q_6	q_7/Q_7	q_8/Q_8	q_9/Q_9	q_{10}/Q_{10}	Q_{11}
q_6/Q_6	1.758/0.679					
q_7/Q_7	0.966/−0.090	1.713/0.678				
q_8/Q_8	1.052/−0.110	1.030/−0.110	2.196/0.945			
q_9/Q_9	0.982/−0.113	0.960/−0.112	0.980/−0.205	1.757/0.647		
q_{10}/Q_{10}	0.999/−0.153	0.952/−0.177	0.998/−0.244	1.048/−0.122	2.087/0.855	
Q_{11}	−0.177	−0.153	−0.245	−0.121	−0.188	0.854

are not tetrahedral (109.47^0). As a result, a form of the matrix A is changed. With due regard for the atomic numbering in Figure 2 , let us find the sets of the independent (q_i) and redundant (Q_i) vibrational coordinates as follows:

$$\delta l_{C_1H_2} \Leftrightarrow q_1, Q_1; \; \delta l_{C_1H_3} \Leftrightarrow q_2, Q_2;$$

$$\delta l_{C_1H_4} \Leftrightarrow q_3, Q_3; \; \delta l_{C_1O_5} \Leftrightarrow q_4, Q_4;$$

$$\delta l_{O_5H_6} \Leftrightarrow q_5, Q_5; \; \delta \varphi_{H_3C_1H_2} \Leftrightarrow q_6, Q_6;$$

$$\delta \varphi_{H_4C_1H_2} \Leftrightarrow q_7, Q_7; \qquad \delta \varphi_{O_5C_1H_2} \Leftrightarrow q_8, Q_8;$$

$$\delta \varphi_{H_4C_1H_3} \Leftrightarrow q_9, Q_9; \qquad \delta \varphi_{O_5C_1H_3} \Leftrightarrow q_{10}, Q_{10};$$

$$\delta \varphi_{O_5C_1H_4} \Leftrightarrow Q_{11};$$

$$\delta \varphi_{C_1O_5H_6} \Leftrightarrow q_{11}, Q_{12}; \; \delta \tau_{H_2C_1O_5H_6} \Leftrightarrow q_{12}, Q_{13};$$

(14)

The matrices A and A^{-1} are represented by relations (15) and (16). Table 3 gives the force field

$$\begin{pmatrix} Q_6 \\ Q_7 \\ Q_8 \\ Q_9 \\ Q_{10} \\ Q_{11} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ -0.9352 & -0.9352 & -0.9562 & -1.0067 & -1 \end{pmatrix} \begin{pmatrix} q_6 \\ q_7 \\ q_8 \\ q_9 \\ q_{10} \end{pmatrix}$$

(15)

$$\begin{pmatrix} q_6 \\ q_7 \\ q_8 \\ q_9 \\ q_{10} \end{pmatrix} = \begin{pmatrix} 0.8459 & -0.1541 & -0.1575 & -0.1658 & -0.1647 & -0.1647 \\ -0.1541 & 0.8459 & -0.1575 & -0.1658 & -0.1647 & -0.1647 \\ -0.1575 & -0.1575 & 0.8389 & -0.1695 & -0.1684 & -0.1684 \\ -0.1647 & -0.1658 & -0.1695 & 0.8214 & -0.1773 & -0.1773 \\ -0.1647 & -0.1647 & -0.1684 & -0.1773 & 0.8238 & -0.1761 \end{pmatrix} \begin{pmatrix} Q_6 \\ Q_7 \\ Q_8 \\ Q_9 \\ Q_{10} \\ Q_{11} \end{pmatrix}$$

(16)

elements for valence angles of the molecular fragment CH_3O, computed using the GAMESS package [10] in the approximation B3LYP/6-311G**. With the use of the relation $K = \tilde{A}^{-1}kA^{-1}$, where A^{-1} is found from (16), a force field of a methanol molecule has been derived for the set of redundant coordinates, the elements of which for valence angles of the fragment CH_3O are also given in Table 3. Correlating the data in Tables 1 and 3, we

note that a value of the force constant K_{HCH} in a methoxy group is somewhat higher (0.647-0.679) than in a methane molecule (0.602). In [16] this force constant has the value 0.76, and for K_{OCH} the empirical force constant is equal to 0.979, being in a good agreement with the values obtained in this work (0.855-0.945). Retention of the local symmetry C_{3v} for the fragment CH_3O was assumed in [16]. As a result, consideration has been given only to two coupling constants for the angles: $K_{HCH/HCH} = -0.1148$ and $K_{HCH/OCH} = -0.091$. According to this work, a symmetry of CH_3O is lowered to C_S and hence, as seen in Table 3, the values of these constants are varied (sometimes considerably) depending on relative positions of the interacting coordinates. Thus, the interaction of HCH angles lying outside the symmetry plane corresponds to $K_{67} = -0.09$, while the interaction of such an angle with a similar one that is in the plane corresponds to $K_{69} = -0.113$. The value of $K_{HCH/OCH}$ is varying from -0.11 to -0.205. Table 4 presents the wave numbers and normal modes computed with sets of the independent and redundant coordinates. As seen from the Table 4, there is a perfect agreement in the computed wave numbers and normal modes become more adequate and obvious with the use of the redundant coordinates.

5. Conclusions

Thus, force fields of methane and methanol molecules computed by the nonempirical quantum-chemical methods with the use of a set of the independent coordinates have been transformed to a set of the redundant coordinates making it possible to derive symmetry of the force fields up to T_d and C_S, respectively. Invariability of the vibrational wave numbers with the use of the transformed force fields supports correctness of the approach, the normal modes and distribution of the potential energy for vibrations being more adequate and obvious. Both the scaled and nonscaled force constants, recalculated

Table 4. Calculated wave numbers and normal modes of methanol.

Experimental values [*]	Independent coordinates		Redundant coordinates	
Wave numbers (cm^{-1})	Wave numbers (cm^{-1})	Normal modes	Wave numbers (cm^{-1})	Normal modes
287.	261.	$-0.67q_{12}$	261.	$1.4Q_{13}$
1033.5	1036.	$0.34q_4 + 0.10q_8 + 0.20q_{11}$	1036.	$0.35Q_4 + 0.19Q_8 - 0.43Q_{12}$
1074.5	1078.	$-0.29q_8 + 0.10q_{10} + 0.25q_{11}$	1078.	$0.15Q_4 - 0.64Q_8 + 0.55Q_{12}$
1145.	1137.	$0.10q_6 - 0.10q_7 - 0.35q_{10}$	1136.	$0.21Q_6 - 0.21Q_7 + 0.76Q_{10} - 0.76Q_{11} + 0.36Q_{13}$
1339.5	1373.	$0.22q_8 - 0.16q_9 - 0.11q_{10} + 0.49q_{11}$	1372.	$0.19Q_6 + 0.19Q_7 + 0.49Q_8 - 0.36Q_9 - 0.23Q_{10} - 0.23Q_{11} + 1.04Q_{12}$
1454.5	1476.	$0.31q_6 + 0.32q_7 - 0.32q_8 + 0.30q_9 - 0.30q_{10}$	1476.	$0.67Q_6 + 0.68Q_7 - 0.68Q_8 + 0.68Q_9 - 0.67Q_{10} - 0.65Q_{11}$
1465.	1484.	$-0.55q_6 + 0.55q_7 + 0.12q_{10} - 0.39q_{12}$	1484.	$-1.19Q_6 + 1.17Q_7 + 0.26Q_{10} - 0.26Q_{11} - 0.84Q_{13}$
1479.5	1499.	$-0.32q_6 - 0.29q_7 + 0.18q_8 + 0.62q_9$	1498.	$0.62Q_6 + 0.67Q_7 - 0.40Q_8 - 1.33Q_9 + 0.25Q_{10} + 0.24Q_{11} - 0.15Q_{12}$
2844.2	2987.	$0.28q_1 + 0.83q_2 + 0.50q_2$	2987.	$0.30Q_1 + 0.87Q_2 + 0.53Q_3$
2970.6	3033.	$-0.12q_1 + 0.58q_2 - 0.86q_2$	3033.	$0.12Q_1 - 0.61Q_2 + 0.90Q_3$
2999.	3096.	$0.99q_1 - 0.20q_2 - 0.27q_2$	3096.	$-1.03Q_1 + 0.21Q_2 + 0.28Q_3$
3681.5	3866.	$-1.03q_5$	3866.	$1.07Q_1$

[*] According to [16]

for a set of the redundant coordinates, may be easily transferred to the allied molecular fragments in large molecules, in particular, with the help of the automatic separation of force constants in standard programs developed for computations of normal vibrations [11].

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