Journal of Spectroscopy and Dynamics

J. Spectrosc. Dyn. 2014, 4: 25

Anharmonic calculations and 3D PES study of the O-H group vibrations in the methanol dimer

G. A. Pitsevich[a,*], A. E. Malevich[a], E. N. Kozlovskaya[a], U. U. Sapeshko[b]

[a] *Belarusian State University, Minsk, Belarus*
[b] *University of Illinois at Chicago, Chicago, USA*

[*]*Author for correspondence: G. A. Pitsevich, email: pitsevich@bsu.by*

Received 30 Nov 2013; Accepted 11 Jan 2014; Available Online 11 Jan 2014

Abstract

Geometry, harmonic and anharmonic vibrations of O-H group of the donor molecule of methanol dimer are studied using ab initio methods employing DFT in conjunction with extended basis set. To describe more accurately proton large amplitude motions, its Cartesian coordinates were used as the vibtrational in order to build the 3D potential energy surface (PES). Using this 3D PES, a flexible Hamiltonian is built numerically and then employed to find the frequencies of the stretching and bending O-H group vibrations. Calculated fundamental frequencies are in reasonable agreement with the corresponding values obtained from the diagonalization of the Hamiltonian matrix. Some discrepancies in the results of the two approaches is largely offset by analyzing the structure of the normal modes and additional accounting of anharmonic interaction of the OH groups vibrations with the rest of the normal modes when 3D PES is used. Comparison of the calculated results with the experimental data presented in the literature was done.

Keywords: Anharmonic calculations of vibrations; 3D PES; Methanol dimer; Hydrogen bond; Hamiltonian matrix

1. Introduction

Methanol (Me) is the simplest representative of nonrigid molecules with internal rotation that is capable to self-associate. Clusters formation of different sizes and configurations leads to appearance of the second type of vibrations with large amplitude. While the first one is associated with the internal rotation around the C-O bonds, the second one is caused by the stretching vibrations of O-H bonds (ν_{OH}^{d}) in the donor molecules of clusters. One can assume that during interpretation of the torsion-rotational spectra of methanol molecule, theoretical approaches to the analysis of internal rotation in molecules were developed [1-3] and so far this type of intramolecular motion attracts the attention of investigators [4,5]. However, we are interested in the second type of the motion with large amplitude. Studies of the spectral and structural properties of complexes and clusters with hydrogen bond (H-bond) receive great attention [6-10]. Methanol dimer (Me_2) is undoubtedly an important object for theoretical studies of spectral manifestations of hydrogen bond formation because of the variety of reasons. Firstly, it contains a small number of both heavy and light atoms, and, therefore, allows to use large enough basis set during calculations and to take into account, within the DFT methods, exchange effects and electron correlation methods. Secondly, since the H-bond in the Me_2 is more related to the weak, the anharmonicity degree of stretching vibrations of the donor O-H bond, although higher than in the acceptor, is still low. Therefore, we expect that the standard model of anharmonicity [11] should adequately predict the values of the corresponding vibrational frequencies. Can the calculations of ν_{OH}^{d} frequencies made by constructing a multidimensional potential energy surfaces (PES) compete with the results of anharmonic calculations of FTIR spectra under these circumstances? Only experiment can give an answer to this question. Hence, the fact that so far reliable experimental studies of FTIR spectra of Me_2 in inert matrices [12-15], as well as in the gas phase [16,17], including size-selected experiments at low temperatures [18-23] is an important aspect. These studies show that the frequency of the maxima of the absorption bands ν_{OH}^{d} can be determined with high accuracy because of their small half-width. As is known [24,25], often the situation in complexes with H-bond is opposite, which greatly complicates the comparison of theoretical and experimental results. Thus, the object of the current study is the calculation of the frequencies of OH group vibrations in Me_2 using anharmonic approximation and by constructing 3D PES followed by comparison with experimental results.

2. Computational methods

Computations of spectral and structural characteristics of Me and Me_2 were performed using quantum-chemical package GAUSSIAN 09 [26] in the approximation B3LYP/cc-pVTZ. It was shown earlier [27,28], that this approximation is quite acceptable for calculations of the structure, FTIR spectra and potential energy surfaces of organic molecules. Calculations of FTIR spectra in harmonic and anharmonic approximations (first approach) were performed for Me and Me_2. In the process of geometry optimization for these compounds, the fact that minima on the potential surface were reached has been supported by the absence of imaginary frequencies in vibrational spectra. Equilibrium configuration of Me_2 is presented in Figure 1. Calculations of the potential surfaces (second approach) were

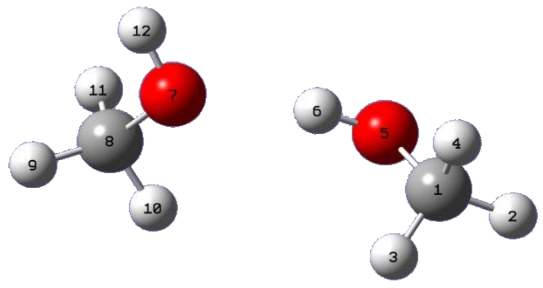

Figure 1. Equilibrium configuration of methanol dimer with indication of atomic numbers.

realized in accordance with [29,30]. For convenience the origin of Cartesian coordinate system in the equilibrium configurations of the complex is placed at H_6 atom (atomic numbers are presented in Figure 1), *X* axis is directed to O_5 atom (along O-H bond). *Y* axis is located in the plane formed by atoms O_5-H_6---O_7, and *Z* axis supplements axes *X* and *Y* to the right-hand triple.

We have computed the complex energies at more than 3500 points by positioning the atom H_6 at the certain nodes of 1D - 3D meshes, without geometrical optimization of the complex for the remaining parameters.

3. FTIR spectra calculations of methanol dimer in harmonic and anharmonic approximations

According to calculations of the equilibrium configuration of Me_2, there is a formation of H-bond with great length of the hydrogen bridge (2.848 Å) and the value of the angle $O_5H_6O_7$ that is far from the flat angle (165.26°) in the dimer. Length of O_5H_6 bond (0.9685 Å) slightly increases in comparison with the length of hydroxyl bond in the monomer (0.9606 Å). Slight differences in geometric parameters of acceptor and donor methanol molecules however lead to significant differences in the force fields and in the frequencies of vibrations. Diagonal force constants of O-H group in Me and Me_2 correspondingly equal to 0.527 and 0.501 H/bor^2. Anharmonicity constants for ν_{OH} and ν_{OH}^{d} modes in Me and Me_2 correspondingly equal to -84.5 and -108.9 cm^{-1}. It should be noted that in harmonic approximation the frequency of O-H stretching vibrations in acceptor molecule (ν_{OH}^{a}) is more than the monomer one (ν_{OH}^{m}) and the frequency of the latter is significantly higher than ν_{OH}^{d} . In anharmonic approximation frequency ν_{OH}^{a} is slightly (by 2 cm^{-1}) higher than ν_{OH}^{m} , at the same time the frequency ν_{OH}^{d} turns out to be more than by 150 cm^{-1} lower. There is a great difference between values of the frequencies for in-plane and especially for out-of-plane bending vibrations of the donor hydroxyl group ($\delta_{OH}^{d(ip)}$ and $\delta_{OH}^{d(oop)}$ respectively). Frequency of the latter one increases to more than two times in the donor molecule of dimer in comparison with the monomer. Calculated frequencies values of harmonic and fundamental vibrations are presented in Table 1.

4. 3D calculations of PES and vibrational frequencies of hydroxyl group

The further calculations were carried out in order to specify the PES associated with the hydrogen atom motion. As well as earlier [29,30] we calculated PES by moving H_6 atom in 3D Cartesian space at the fixed positions of the other atoms of the complex. The position of the Cartesian coordinate system is described above. The motion of the hydroxyl H atom along the X axis is associated with the stretching vibrations of the hydroxyl group. In-plane and out-of-plane bending vibrations of O-H group can be associated with the motion along Y and Z axes. It is obvious that for 1D and 2D calculations such a correspondence is true only in the finite interval of ΔY and ΔZ. However it is clear that in the case of 3D calculations it doesn't matter which of the two coordinate sets ($l_{OH}, \varphi_{COH}, \tau_{OCOH}$ or ΔX, ΔY, ΔZ) is used for the description of the hydroxyl group vibrations. Potential energy values were calculated in some nodes of the three-dimensional grid for the intervals of H_6 shifting from the equilibrium position from -0.8 Å to +0.5 Å along X axis, from -1.0 Å to +1.0 Å along Y and Z axes. For the values ΔX from -0.8 Å to +0.5 Å with the step 0.1 Å (a) we have calculated the energy in the nodes on the planes which are perpendicular to the X axis. For each plane the chosen values ΔZ equal to -1.0,-0.9,-0.7, -0.5, -0.3,-0.2, -0.1, 0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9 and 1.0 Å (b). For each of these values ΔZ the values ΔY were chosen to be equal to -1.0,-0.9,-0.7, -0.5, -0.3,-0.2, -0.1, 0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9 and 1.0 Å (c). Thus, the potential energy was calculated in more than 3500 points. Then, by the interpolation methods using the program set Mathematica [31] the energy was calculated in all nodes of the parallelepiped with the sizes $\Delta X \cdot \Delta Y \cdot \Delta Z = 1.3 \cdot 2.1 \cdot 2.1$ Å^3 and with the step 0.1 Å along each of the axes. This process was realized in two stages. At the first stage we found the energy in the points with the coordinate values ΔY = -0.8, -0.6, -0.4, +0.4, +0.6, +0.8 Å for each of the calculated earlier (b) values of ΔZ . It was made for each of fourteen planes by the interpolation with the splines of the third order along the directions parallel to the Y axis. At the second stage the energy along the directions which are parallel to the Z axis in the nodes with the coordinates ΔZ = -0.8,-0.6,-0.4,+0.4,+0.6,+0.8 Å was similarly determined. Thus the potential energy values in 6174 nodes of the three-dimensional grid were determined. At this in more than 3500 nodes the energy was found directly by quantum-chemical calculations, and in more than 2600 nodes – by the interpolation.

In order to determine the vibrational frequencies for the hydroxyl group it was necessary to solve the Schrodinger equation:

$$-R\left(\frac{\partial^2\Psi(x,y,z)}{\partial x^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{\partial^2\Psi(x,y,z)}{\partial z^2}\right) + U(x,y,z)\Psi(x,y,z) = E\Psi(x,y,z) \qquad (1)$$

Table 1. Frequencies values of harmonic, fundamental and overtones O-H vibrations of Me and Me_2.

Vibration mode	Me				Me_2 (acceptor)				Me_2 (donor)			
	Mode number N	Harmonic wave number (cm^{-1})	Fundamental wave number (cm^{-1})	Overtone wave number (cm^{-1})	Mode number N	Harmonic frequency (cm^{-1})	Fundamental frequency (cm^{-1})	Overtone frequency (cm^{-1})	Mode number N	Harmonic wave number (cm^{-1})	Fundamental wave number (cm^{-1})	Overtone wave number (cm^{-1})
$\tilde{\nu}_{OH}$	1	3829.9	3657.0	7145.0	1	3835.5	3654.9	7137.7	2	3681.7	3500.5	5813.7
δ_{OH}^{ip}	6	1374.9	1329.3	2644.2	16	1368.1	1315.1	2612.9	15	1431.5	1402.2	2780.2
δ_{OH}^{oop}	12	299.8	261.7	464.4	24	311.4	367.7	666.7	23	686.4	534.6	937.8

Table 2. The frequencies of O-H vibrations, calculated in different approximations of the theory.

Vibration type	**Approximation used for the frequency calculation**								
	1DX (cm^{-1})	**1DY (cm^{-1})**	**1DZ (cm^{-1})**	**2DXY (cm^{-1})**	**2DXZ (cm^{-1})**	**2DYZ (cm^{-1})**	**3DXYZ (cm^{-1})**	**Anharm. (cm^{-1})**	**PED**
$\tilde{\nu}_{OH}$	3485.3			3487.8	3508.8		3511.8	3500.5	100%q_{OH}
δ_{OH}^{ip}		1392.9		1310.5		1374.2	1342.5	1402.2	59% δ_{OH}^{ip} +38% δ_{CH_3}
δ_{OH}^{oop}			892.6		669.3	872.3	652.8	534.6	21% δ_{OH}^{oop} +20% $q_{O\cdot\cdot H}$ + +20% $\delta_{OH\cdot\cdot O}$ +15% $\tau_{COH\cdot\cdot O}$

where $R=\frac{\hbar^2}{2\mu l_0^2}=17.7889919$ $cм^{-1}$; $\mu=\frac{M_H M_O}{M_H+M_O}$ - reduced mass of oxygen and hydrogen atoms; $x=\frac{\Delta X}{l_0}, y=\frac{\Delta Y}{l_0}, z=\frac{\Delta Z}{l_0}$ - dimensionless variables ($l_0=1$ Å).

Using the reduced mass instead of hydrogen atom mass, we take into account the fact that it is the motion of valence-bond oxygen atom, but not the motion of a whole dimer, compensates the momentum associated with the vibrational motion of H_6 atom along each of the axis. The equation (1) was solved numerically using the program set [31]. The way of the solution is partly described in [29,30] and in more detail in [32]. The results of the calculations are presented in Table 2.

We can additionally take into account the anharmonic interaction of the analyzed modes with other normal modes using the expression (2) which was used for the free complex in [29,30]:

$$\tilde{\nu}_A^{fund}=\tilde{\nu}_A^{3D}+\frac{1}{2}\sum_{j=1}^{N}\chi_{A,j},\ A=2,15,23;\ j\neq 2,15,23 \tag{2}$$

where χ_{ij} - components of the matrix of anharmoniciry constants. Since $\frac{1}{2}\sum_{j}^{N}\chi_{2,j}=+23.9$; $\frac{1}{2}\sum_{j}^{N}\chi_{15,j}=-36.8$ and $\frac{1}{2}\sum_{j}^{N}\chi_{23,j}=-83.7$ cm^{-1} $(j\neq 2,15,23)$, then the values of the frequencies of stretching, in- and out-of-plane bending vibrations of a hydroxyl group are 3535.7, 1305.7 and 569.1 cm^{-1}, respectively.

5. Results and Discussion

The wavenumbers of vibrations $\nu_{OH}^{d}, \delta_{OH}^{d(ip)}$ and $\delta_{OH}^{d(oop)}$ calculated in anharmonic approximation appear to be equal to 3500.5, 1402.2 and 534.6 cm^{-1}, while the values of corresponding wavenumbers obtained using the second approach are equal to 3511.8, 1342.5 and 652.8 cm^{-1}. While comparing these results, we should keep in mind some features of the used approaches. Calculation in the anharmonic approximation is using the full set of vibrational degrees of freedom. And in harmonic approximation the first step in the calculation of the normal modes takes into consideration the interaction of elementary oscillators of the same symmetry (in particular, coordinate of a symmetry can be considered as such oscillator). The second step takes into account the anharmonic interaction of normal modes. This is an undoubted advantage of anharmonic calculations. Forming the PES allows to precisely interpret the dependence of potential and kinetic energy of some coordinates. However, the number of using coordinates is abruptly limited. It is necessary to understand that when calculations of nD is in process, in spite of the fact that the values of vibrational coordinates are taken as equal to zero, the result of the calculations will also depend on the choice of the remaining 3$\mathcal{N}$-n-6 vibrational coordinates ($\mathcal{N}$ is a number of atoms in the molecule or dimer). On the other hand, n vibrational coordinates that are using while forming the PES not necessarily have to be natural coordinates. It may be some of their linear combinations. With that said, we should first of all note that according to the data of harmonic calculations modes N2, N15 and N23 (numbering of the modes see in Table 1) are different in the words of contribution degree of the natural coordinates ν_{OH}^{d}, $\delta_{OH}^{d(ip)}$ and $\delta_{OH}^{d(oop)}$ to the potential energy distribution (PED) of corresponding vibrations. The mode N2 is completely localized (contribution of the ν_{OH}^{d} to PED of the second mode is 100%). For N15 and N23 modes the situation is different. Contribution $\delta_{OH}^{d(ip)}$ to PED of the mode N15 is 59%, and contribution of the $\delta_{OH}^{d(oop)}$ to PED of the mode N23 is only 21%. Thus, in case of mode N2, we should only additionally consider its anharmonic interaction with other normal modes (besides the interaction with the N15 and N23 normal modes, that is fully taken into account in 3D calculations). Taking into consideration this interaction and using the expression (5) we can obtain the final value for the wavenumber of the vibration ν_{OH}^{d} - 3535.7 cm^{-1}. What does the experiment say about the frequency of these vibrations? We'll need size-selected experimental results in nonpolar media, and even better in a vacuum. In that respect the results of the spectral studies of methanol dimer in matrix isolation are of a interest. In papers [12-15] FTIR spectra of some methanol clusters were obtained in argon and nitrogen matrices at temperatures 7-20 K. Frequencies of the maxima of absorption bands that assigned to the ν_{OH}^{d} are in the interval 3490 -3525 cm^{-1}. It should be noted that specified problems while interpretating the matrix spectra arise due to the presence of several methanol dimer conformers in the sample, and also due to the "site"-effect. Furthermore, despite the fact that the inert gases are the least polar media, they are still able to polarize under the action of the captured molecules, and hence are able to influence on the frequencies of fundamental vibrations of the investigated molecules. In that respect the results of the studies of methanol clusters in the gas phase are of a great interest. In earlier work [16] FTIR spectrum of methanol vapor was studied, but its results are not very informative. Later [17] FTIR spectrum of methanol vapor was obtained with high resolution. Authors assigned the absorption band 3411 cm^{-1} to the ν_{OH}^{d} vibration. However, absence of the selections of the clusters by sizes and presence of the rotational structure in vibrational absorption bands prejudice this assignment. Lately a number of experimental researches were carried out [18-23], where after a preliminary size-selections of the clusters FTIR spectrum of methanol dimer in the gas phase at very low temperatures (about 4K) was registered, which allows to obtain the vibrational absorption bands without rotational structure. The results of these works are surprisingly close (band with the frequency of the maximum close to 3575 cm^{-1} was assigned to the ν_{OH}^{d} vibration), although they were obtained in significantly different conditions of clusters selection. This fact is practically eliminates doubts about their results. Thus, we can say that ν_{OH}^{d} frequency computed in anharmonic approximation (3500.5 cm^{-1}) has a good agreement with the experimental one, but the value that was computed by constructing 3D PES (3511.8 cm^{-1}), and especially the value obtained by taking into consideration advantages of both approaches (3535.7 cm^{-1}) are closer to the experimental one.

Lets turn to the analysis of mode N15. The difference in the calculated frequency values of this mode obtained using both methods is significant. However, we should consider the fact that in-plane bending vibration of the donor hydroxyl group - $\delta_{OH}^{d(ip)}$ is mixed with symmetric rock vibration of C-H bonds in methyl group ($\delta_{CH_3}^{s(rock)}$). There is also another mode (N19) with the frequency 1097.2 cm^{-1} in PED of which contribution of the $\delta_{CH_3}^{s(rock)}$ is dominated, but at the same time there is also a significant (up to 30%) contribution of $\delta_{OH}^{d(ip)}$ vibration. This kind of dynamic and force interaction between the vibrations of two oscillators with close energies leads to their mixing and increase of the frequency gap between them. Of course, this interaction is not considered in any way in the approach that is using 3D PES. Hence, for more objective comparison of the calculations results of the frequency of this mode in two cases, we should determine the frequency of $\delta_{OH}^{d(ip)}$ vibration without interaction with $\delta_{CH_3}^{s(rock)}$. We can approximately estimate the frequencies of non-interacting $\delta_{OH}^{d(ip)}$ and $\delta_{CH_3}^{s(rock)}$ vibrations by making two additional calculations for fundamental vibrations of methanol dimer in anharmonic approximation, with substituting in the first case the masses of the hydrogen atoms in methyl group of the donor molecule for tritium masses; and in the second case – by making the same substitution for the hydroxyl hydrogen atom. After making these calculations we obtained the frequencies $\delta_{OH}^{d(ip)}$ and $\delta_{CH_3}^{s(rock)}$ vibrations of the following values: 1354.0 and 1209.0 cm^{-1}. We can see that the unperturbed by the interaction modes are actually closer to each other (in terms of frequency), and, besides, the frequency of the unperturbed vibration (1354.0 cm^{-1}) is significantly better goes with the corresponding value obtained using the second approach (1305.7 cm^{-1}). Taking into account the correction for the oscillators interaction we obtain the frequency value 1353.7 cm^{-1} for the second approach, while the first approach gives the value 1402.2 cm^{-1}. What does the experiment say? Unfortunately in [18-23] only O-H stretching vibrations region was analyzed. So we have to rely on the results presentes in [12-15]. According to the data obtained in these papers, values of the absorption bands frequencies caused by this vibration are in the range 1359 -1405 cm^{-1}. Precise value depends on the matrix type, and in the less polar (argon) matrix frequency of corresponding band is lower than in the more polar (nitrogen) matrix. One can assume that in a vacuum the value of the maximum of corresponding absorption band will be closer to the low-frequency edge of the refferd above spectral range.

Lets proceed to the consideration of the mode N23 in the vibrational spectrum of the methanol dimer. As noted above, this is without a doubt delocalized vibration. So how are the results of two approaches (534.6 and 569.1 cm^{-1}) quite close? Despite the fact that contribution of $\delta_{OH}^{d(oop)}$ in PED of this mode is small, there is no comparable contribution of $\delta_{OH}^{d(oop)}$ in PED of any other modes. Analysis of PED of mode N23 denotes that the remaining and key contribution in PED is made by the natural coordinates, which define intermolecular movement - changing of the hydrogen bond length and valence O-H---O angle in the hydrogen bridge. However, we can say that the influence of the changing of these coordinates adequately take into consideration in the 3D approach while displacing H_6 along X, Y and Z axes. This, in our view, determines a good agreement between two approaches, especially after additional accounting of anharmonic interaction of mode N23 with other (besides of N2 and N15) normal modes. Now lets refer to the experiment (data in the papers [12-15]). Value of the frequency of maximum of the absorption band due to this vibration in nitrogen matrix (according to [13]) is in the range 572 - 624 cm^{-1} depending on the conformers structure. One can assume that while decreasing polarity of the medium the frequency of the maximum of corresponding band will experience a red shift. However, in this case more thorough experimental investigation are very desirable.

6. Conclusions

Frequencies of stretching and bending vibrations of the donor hydroxyl group in methanol dimer were calculated using two independent approaches. The weakness of the hydrogen bond in the dimer and, as a consequence, moderate anharmonicity of the vibrations of O-H bond causes good agreement between vibrational frequencies obtained using both approaches. Precise experimental data on the frequency of the stretching vibration of the donor hydroxyl group in vacuum (3575.0 cm^{-1}) that are presented in the literature allow us to consider the results of the calculations in anharmonic approximation (3500.5 cm^{-1}) and results obtained by constructing 3D PES (3511.8 cm^{-1}) satisfactory enough. The previously used method, which combines the advantages of both approaches [29,30] allows to bring the calculated value of the vibrational frequency (3535.7 cm^{-1}) even closer to the experimental. Calculated values of the frequencies of bending vibrations of the donor hydroxyl group using two approaches also have good agreement with each other and with the experimental data obtained for samples in matrix isolation. In the latter case, however, experimental studies of methanol dimer in the gas phase at low temperatures are required. We should admit that the success of the second approach is largely due to the good choice of coordinates which describe the vibrational motion of a hydroxyl group. It allowed to significantly simplify the form of the Schrödinger equation, which means the simplification of its solutions.

Acknowledgments

This study was supported by the State Foundation for Basic Research of Belarusian Republic (Grant No. F13K-064)

References

1. J. S. Koehler, D. M. Dennison, Phys. Rev. 57 (1940) 1006.
2. D. G. Burkhard, D. M. Dennison, Phys. Rev. 84 (1951) 408.
3. E. V. Ivash, D. M. Dennison, J. Chem. Phys. 21 (1953) 1804.
4. L. H. Xu, J. T. Hougen, J. M. Fisher, R. M. Lees, J. Mol. Spectrosc. 260 (2010) 88.
5. A. E. Hilali, L. H. Coudert, I. Konov, S. Klee, J. Chem. Phys. 135 (2011) 194309.
6. G. Pitsevich, A. Malevich, I. Doroshenko, E. Kozlovskaya, V. Pogorelov, V. Sablinskas, V. Balevicius, Specrochim. Acta A 120 (2014) 585.
7. A. Foldes, C. Sandorfy, J. Mol. Spectrosc. 20 (1966) 262.
8. L. C. Remer, J. H. Jensen, J. Phys. Chem. A 104 (2000) 9266.
9. T. Lankau, C. H. Yu, PCCP 9 (2007) 299.
10. S. Kopec, P. Ottiger, S. Leutwyler, H. Koppel, J. Chem. Phys. 137 (2012) 184312.
11. G. Herzberg, Molecular Spectra and Molecular Structure, Specra of Diatomic Molecules, D. Van Nostrand Company, Inc., Toronto Vol. 1 (1950) p. 93.
12. A. J. Barnes, H. E. Hallam, Trans. Faraday Soc. 66 (1970) 1920.
13. S. Coussan, A. Loutellier, J. P. Perchard, S. Racine, A. Peremans, A. Tadjeddine, W. Q. Zheng, Chem. Phys. 223 (1997) 279.
14. S. Coussan, Y. Bouteiller, A. Loutellier, J. P. Perchard, S. Racine, A. Peremans, W. Q. Zheng, A. Tadjeddine, Chem. Phys. 219 (1997) 221.
15. J. P. Perchard, Z. Mielke, Chem. Phys. 264 (2001) 221.
16. R. G. Inskeep, J. M. Kelliher, P. E. McMahon, B. G. Somers, J. Chem. Phys. 28 (1958) 1033.
17. V. M. Mitev, B. Stefanov, L. M. Ivanov, G. M. Georgiev, J. Mol. Struct. 129 (1985) 11.
18. F. Huisken, A. Kulke, C. Laush, J. M. Lisy, J. Chem. Phys. 95 (1991) 3924.
19. T. Haber, U. Schmitt, M. A. Suhm, Phys. Chem. Chem. Phys. 1 (1999) 5573.
20. R. A. Provencal, J. B. Paul, K. Roth, C. Chapo, R. N. Casaes, R. J. Saykally, G. S. Tschumper, H. F. Schaefer III, J. Chem. Phys. 110 (1999) 4258.
21. Y. J. Hu, H. B. Fu, E. R. Bernstein, J. Chem. Phys. 125 (2006) 154306.
22. R. W. Larsen, P. Zielke, M. A. Suhm, J. Chem. Phys. 126 (2007) 194307.
23. H. L. Han, C. Camacho, H. A. Witek, Y. P. Lee, J. Chem. Phys. 134 (2011) 144309.
24. V. Balevicius, K. Aidas, I. Svoboda, H. Fuess, J. Phys. Chem. A 116 (2012) 8753.
25. G. M. Florio, E. L. Sibert III, T. S. Zwier, Farad. Discuss. 118 (2001) 315.
26. 26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, C. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.1, Gaussian Inc., Wallingford CT (2009).
27. G. A. Pitsevich, A. E. Malevich, Am. J. Chem. 2 (2012) 312.
28. G. A. Pitsevich, M. Shundalau, J. Spectrosc. Dyn. 2 (2012) 15.
29. G. A. Pitsevich, V. E. Pogorelov, I. U. Doroshenko, A. Malevich, V. Sablinskas, V. Balevicius, J. Spectrosc. Dyn. 3 (2013) 19.
30. G. A. Pitsevich, A. Malevich, V. Sablinskas, I. U. Doroshenko, V. E. Pogorelov, E. N. Kozlovskaya, V. Balevicius, Vestnik of the Foundation for Fundamental Research, 63 (2013) 80.
31. Mathematica, Wolfram Research, Inc., http://www.wolfram.com/mathematica/.
32. G. A. Pitsevich, A. E. Malevich, OPJ 2 (2012) 332.

Cite this article as:

G. A. Pitsevich *et al.*: **Anharmonic calculations and 3D PES study of the O-H group vibrations in the methanol dimer.**
J. Spectrosc. Dyn. 2014, **4:** 25